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ATMOSPHERIC SCAVENGING OF HYDROCHLORIC ACID

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Prepared by

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for George C. Marshall Space Flight Center

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16. ABSTRACT <p>The scavenging of hydrogen chloride from a solid rocket exhaust cloud was investigated by an experiment in which water drops were caused to fall at terminal velocity through a confined solid rocket exhaust cloud. The water drops were collected and analyzed to determine the amount of HCl captured during fall. The concentration of HCl within the chamber during the time of the scavenging experiment was measured by means of bubblers. Tests showed that the measured chamber HCl concentration, together with the measured HCl deposition on the chamber walls, accounted for 81 to 94% of the theoretical HCl. This mass balance lends confidence to the measurement techniques.</p> <p>It was found that the HCl captured by water drops during fall is approximately one-half that predicted by the classical Frössling correlation, which applies to water drops falling through a 'clean' HCl cloud. No effect of humidity on the scavenging efficiency was detected. The humidity range covered was 69-98%.</p> <p>The experimental scavenging results for 0.9 mm drops was extended mathematically to cover natural rains. An example calculation for scavenging of HCl from a solid rocket exhaust cloud was given using an idealized Kennedy Space Center rain cycle. This cycle contains an aggregate of two hours of light rain (6.4 mm/hr), 15 minutes of medium rain (24 mm/hr), and five minutes of heavy rain (55 mm/hr). It was calculated that this rain cycle would reduce the cloud HCl concentration to 20.6% of its value in the absence of rain.</p>					
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FOREWORD

This is the final report on IITRI's Project No. C6312 entitled "Atmospheric Scavenging of Hydrochloric Acid". This report is intended to be self-contained. It includes the key information from the four monthly reports issued prior to this report, as well as from IITRI's previous project of the same title, Project No. C6281.

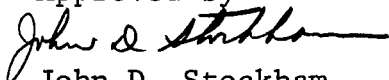
The authors are happy to acknowledge the many suggestions received in the course of this work from Drs. L. L. DeVries and J. B. Stephens of NASA/MSFC. These suggestions resulted in improved experimental procedures and, ultimately, in more reliable results. In particular, a mass balance of HCl was attempted and achieved; this increased our confidence in the HCl measurement techniques used in this work.

The authors also acknowledge the help of the Jet Propulsion Laboratory, particularly Mr. Leon Strand, in supplying the rocket motors used in this work. Ms. Anne O'Donnell of IITRI is thanked for conducting chloride ion and pH measurements on the several scores of samples.

The primary record of this work is contained in IITRI Logbooks C21841 and C21849.

The authors have enjoyed their association with scientists at Marshall Space Flight Center and are pleased to present this contribution to assessing the environmental impact of the Space Shuttle program.

Approved by




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Respectfully submitted,

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TABLE OF CONTENTS

	<u>Page No.</u>
1. INTRODUCTION.	1
2. EXPERIMENTAL APPARATUS.	3
2.1 Spherical Aerosol Chamber.	3
2.2 Rocket Motor and Exhaust Cloud	6
2.3 Rain Simulator	9
2.4 Rain Collection and Reference Blank.	15
2.5 Hydrogen Chloride Concentration.	17
3. EXPERIMENTAL PROCEDURE.	19
4. EXPERIMENTAL RESULTS.	20
4.1 Test Conditions.	20
4.2 Scavenging Test Results.	20
5. EXTENSION TO SCAVENGING BY A POST-LAUNCH RAIN .	26
6. EXAMPLE APPLICATION: HYPOTHETICAL TITAN LAUNCH AT KENNEDY SPACE CENTER	30
7. CONCLUSIONS	34
8. RECOMMENDATIONS	37
REFERENCES	38
Appendix A -- TEMPERATURE, PRESSURE, HCl, AND Al ₂ O ₃ HISTORY FOR THE CONFINED ROCKET EXHAUST CLOUD.	40
Appendix B -- MASS BALANCES FOR ROCKET EXHAUST HCl AND Al ₂ O ₃	61
Appendix C -- ABSORPTION OF HCl ON VARIOUS SURFACES.	71

LIST OF TABLES AND FIGURES

<u>Table</u>		<u>Page No.</u>
1	Results of Raindrop Generator Test	11
2	Test Conditions for Scavenging Tests	21
3	Results of the Scavenging Tests.	22
4	Gunn-Kinzer Data on Raindrop Fall Velocity .	27
5	Idealized Model of a Post-Launch Rain.	31
6	Reduction of HCl Concentration in a Solid Rocket Exhaust Cloud Due to the Idealized. .	32
<u>Figure</u>		
1	Chamber and Apparatus for Scavenging Test. .	4
2	Top View Chamber Schematic with Positions of Internal Experiments.	5
3	Rocket Motor Mounting within 5.49 m (18 ft) Spherical Chamber.	7
4	Rocket Firing Pressure Traces.	8
5	Drop Generator in Rayleigh Breakup Mode. . .	13
6	Spreading of Raindrops from Rain Simulator Over Entire Length of Fall	14
7	Rain Field 2.7 m Below Raindrop Generator. .	16
8	Experimental Scavenging Results.	24
9	Effect of Scavenging Upon Exhaust Cloud Centroid Concentration	33

ATMOSPHERIC SCAVENGING OF HYDROCHLORIC ACID

1. INTRODUCTION

This report presents the results of work done to determine the washout of HCl from solid rocket exhaust clouds by natural rain. Washout involves several microphysical processes within the cloud, including the solubility of HCl in raindrops, the diffusion of HCl to falling drops, and the number, size, and fall velocity of the raindrops (1,2,3,4).

Another potentially important microphysical process in HCl washout was suggested by the work of Gillespie and Johnstone (5), who found that the threshold for water droplet formation is lowered to 78% relative humidity by the presence of HCl gas and small NaCl particles. The droplets formed were of approximately 5 μm diameter -- too small to precipitate, but large enough to dissolve a large fraction of the total HCl. Thus, at humidities in excess of 78%, washout of cloud droplets containing HCl must be considered in addition to the washout of gaseous HCl.

The importance of HCl partitioning between the gas phase and the cloud droplets may be seen by comparing Kerker and Hampl's (6) estimates for the washout coefficient for small particles (1.6×10^{-5} - $2.5 \times 10^{-5} \text{ sec}^{-1}$) to Pellett's (7) estimate of HCl gas washout from a droplet-free cloud. Over an equivalent range of rain intensities, Pellett's estimate was 1.11×10^{-4} to $6.0 \times 10^{-4} \text{ sec}^{-1}$. This indicates that the formation of small droplets within the cloud would sharply decrease the rate of scavenging of HCl by rain.

The large number of aluminum oxide particles produced during combustion of solid rocket fuel augment the naturally present sea-salt and other particles as potential cloud droplet nuclei. The nucleating efficiency of aluminum oxide particles, however, is unknown.

The lack of detailed data on the microphysical processes within a solid rocket exhaust cloud dictated an experimental approach to the determination of HCl washout. Thus, the main part of the work reported here was an experiment in which direct measurement was made of the HCl acquired by water drops falling at terminal velocity through an actual solid rocket exhaust cloud.

The apparatus used in the work is described in Section 2 of this report. The procedure and main results are presented in Sections 3 and 4, respectively. Section 5 extends these results to the scavenging of HCl in a post-launch rain, and Section 6 presents an example scavenging calculation based on a typical Kennedy Space Center rain cycle. The conclusions from this work are summarized in Section 7.

Three appendices are attached to this report, presenting data on the heat balance and the HCl and Al_2O_3 mass balances for the confined rocket exhaust cloud. Preliminary data on the absorption of HCl by various surfaces are also presented.

2. EXPERIMENTAL APPARATUS

The main part of this work was an experiment in which water drops at terminal fall velocity were exposed to a solid rocket exhaust cloud and the amount of HCl acquired by the drops was determined by direct measurement. The experimental equipment included a spherical chamber, rain simulator, rocket motor, and associated instrumentation. The purpose of the equipment was to confine the rocket exhaust cloud to facilitate the rain scavenging experiment. The associated instrumentation characterized the exhaust cloud and was not concerned with the rain scavenging experiment.

2.1 Spherical Aerosol Chamber

The spherical aerosol chamber was fabricated from welded steel plate and was 5.49 m in diameter. The chamber is rated for 5.44 atmospheres of gauge pressure. The volume of the spherical chamber was 86.47 m^3 . The inside surface of the chamber was coated with Plasite #7122, an epoxy-phenolic material resistant to acids and an oil-base enamel. Schematic drawings of the chamber apparatus layout for the experiments are shown in Figures 1 and 2.

In the last three tests conducted, the HCl concentration within the chamber was lowered by partially venting the chamber prior to operating the scavenging experiment. Venting was accomplished by use of the normal chamber venting system. Valves were opened to allow room air to be drawn into the chamber by the action of an exhaust blower connected to the chamber. The inlet and outlet were on opposite walls of the chamber. Thorough mixing was observed during venting by the motion of the Al_2O_3 dust cloud within the chamber. The chamber underpressure during venting was $0.66 \text{ cm H}_2\text{O}$. The venting flow rate was estimated from the dimensions of the inlet pipe. This permitted a preliminary estimate of the venting time required to achieve a specified dilution. In all cases, the dilution actually achieved was determined by

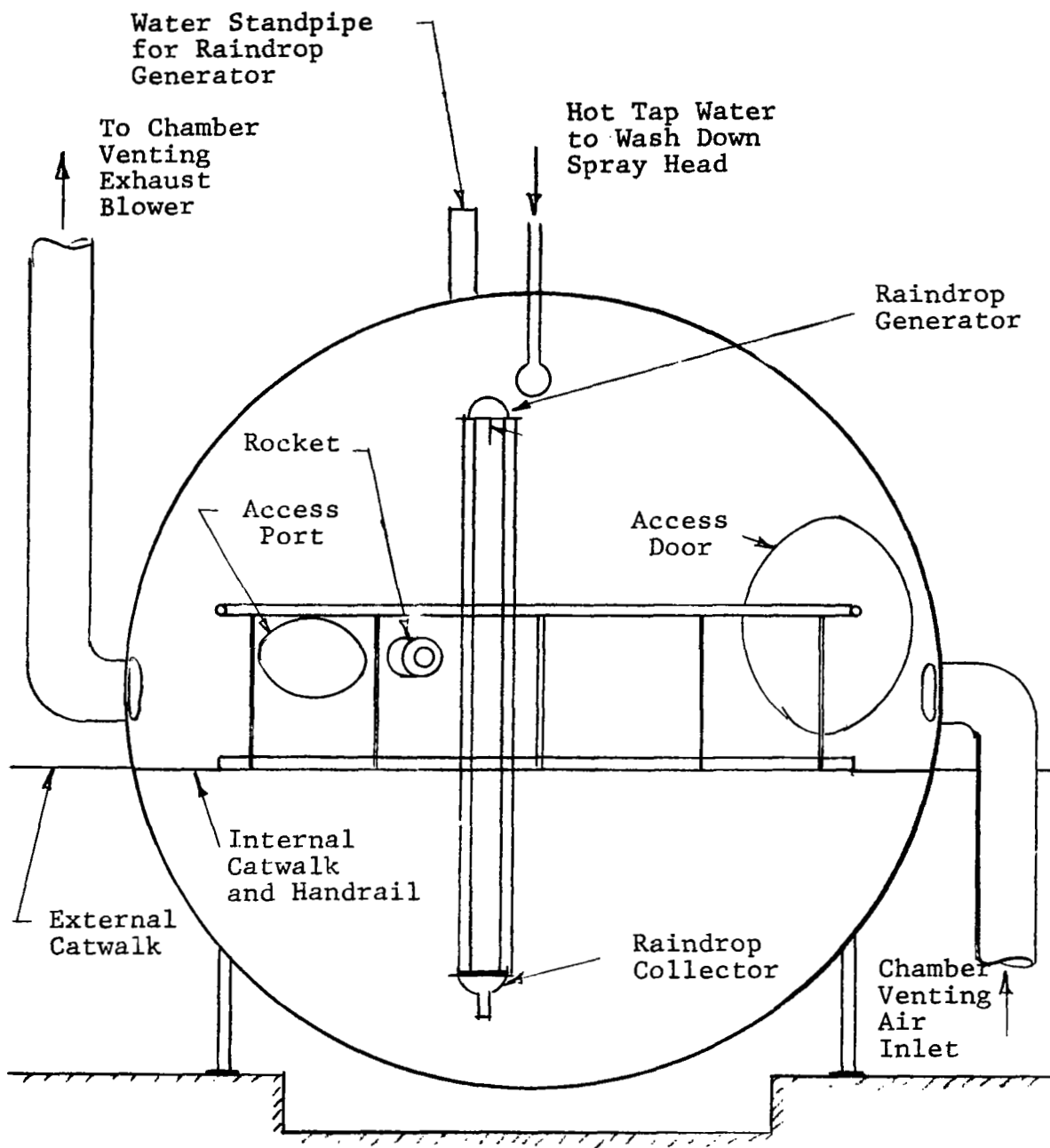


Figure 1

CHAMBER AND APPARATUS FOR SCAVENGING TESTS

Cross-sectional view of elevation.

Chamber diameter = 5.49 m

Raindrop fall distance = 2.8 m

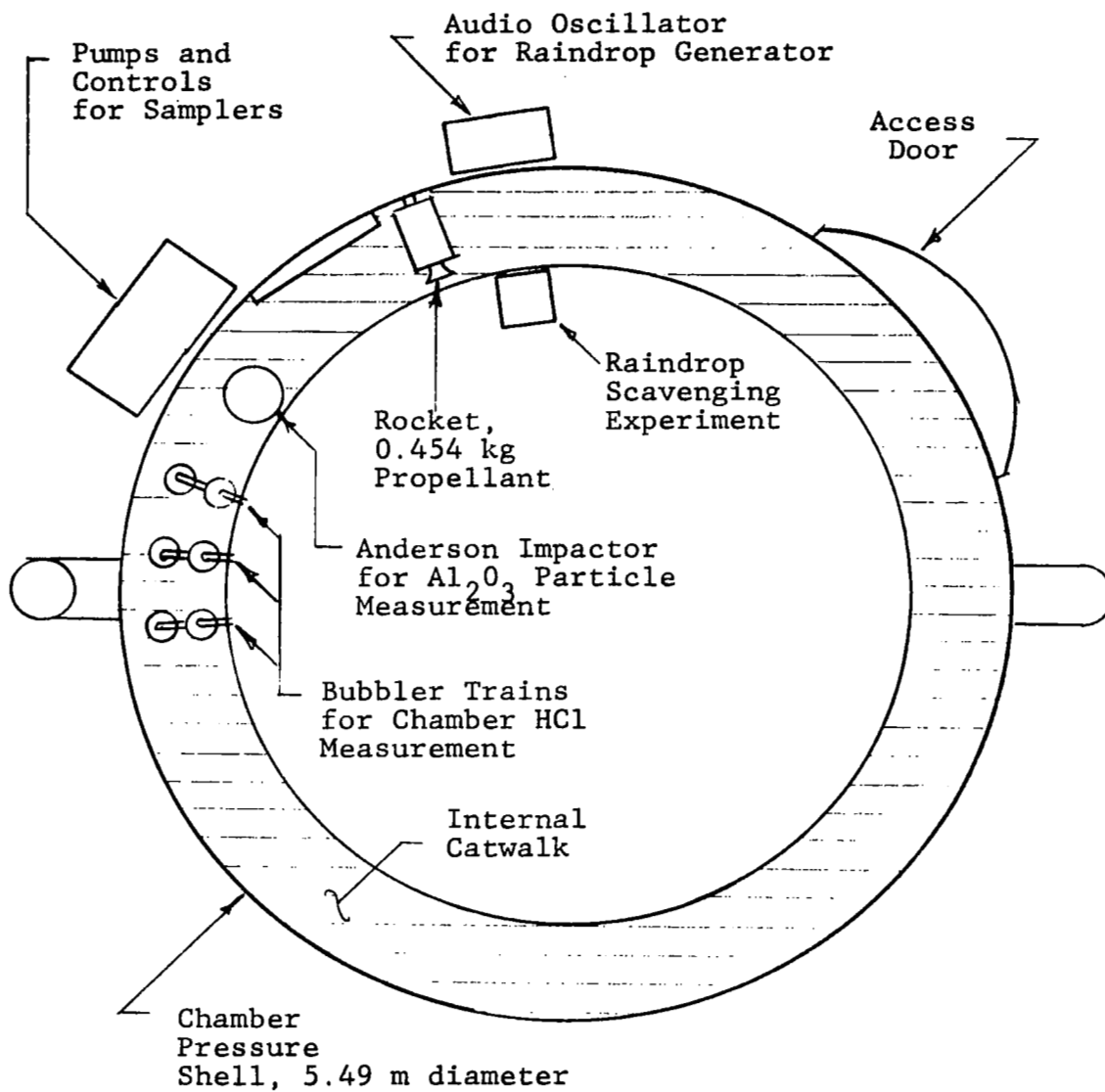


Figure 2
TOP VIEW CHAMBER SCHEMATIC WITH POSITIONS OF
INTERNAL EXPERIMENTS

air samples taken at the conclusion of venting. The relative humidity at the conclusion of venting, however, was estimated from the difference between the post-firing chamber humidity and the room humidity, and the venting time and flow rate.

2.2 Rocket Motor and Exhaust Cloud

The rocket motors used in these scavenging tests were obtained from the Jet Propulsion Laboratory in Pasadena, California*. The pertinent JPL drawings are D9041893 and D9041612.

Each rocket motor contained an approximately 0.454 kg bonded-in propellant grain, with a 3.8 cm diameter axial perforation. The grain outside diameter and length were both approximately 7.6 cm. The propellant composition was (8)

Ammonium perchlorate	70% by weight
Aluminum	16%
PBAN	14%

The rocket exhaust gases discharged through a converging-diverging nozzle with an expansion ratio of 4:1 and a throat diameter of 0.927 cm. A spent rocket motor mounted within the chamber is seen in Figure 3.

Records of the rocket motor combustion chamber pressure were obtained in each test. Examples of pressure traces are given in Figure 4 for two rockets. As can be seen, variations in burn time do exist and are on the order of 15%. The burn time variation indicates the variation of the exhaust cloud mass generated,

The spherical test chamber contains approximately 102 kg of air prior to rocket ignition. Since the rocket motor itself was comprised of 0.454 kg of propellant, the dilution

* Arrangements for the delivery of these rockets to IITRI were made by Mr. John Kaufman and Mr. Robert Turner of NASA/George C. Marshall Space Flight Center, and Mr. Leon Strand of the Jet Propulsion Laboratory.

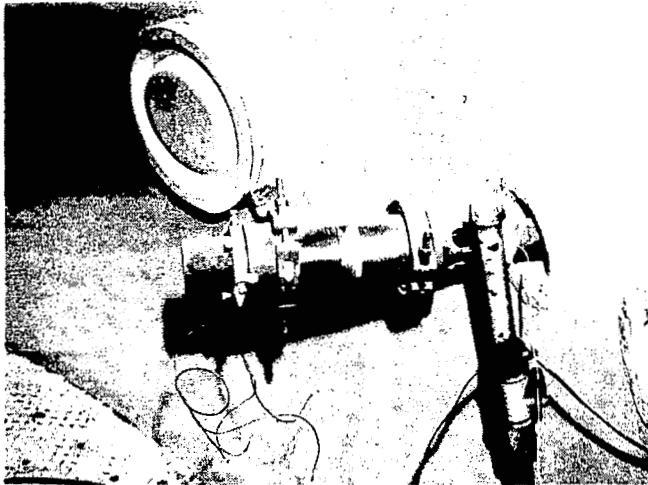
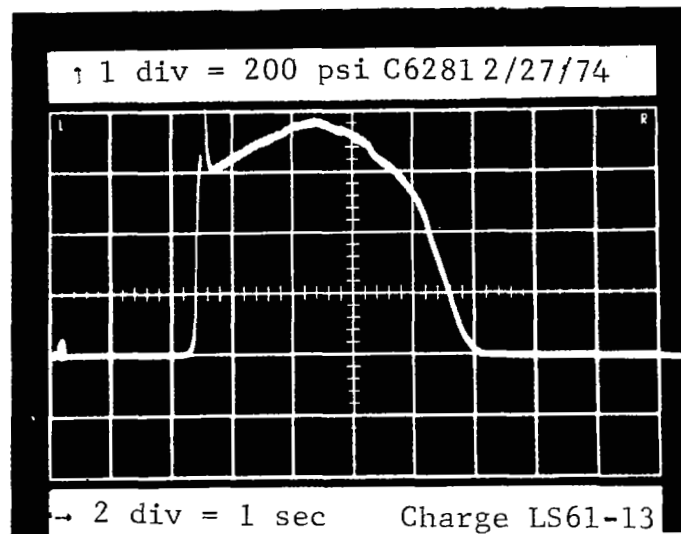


Figure 3

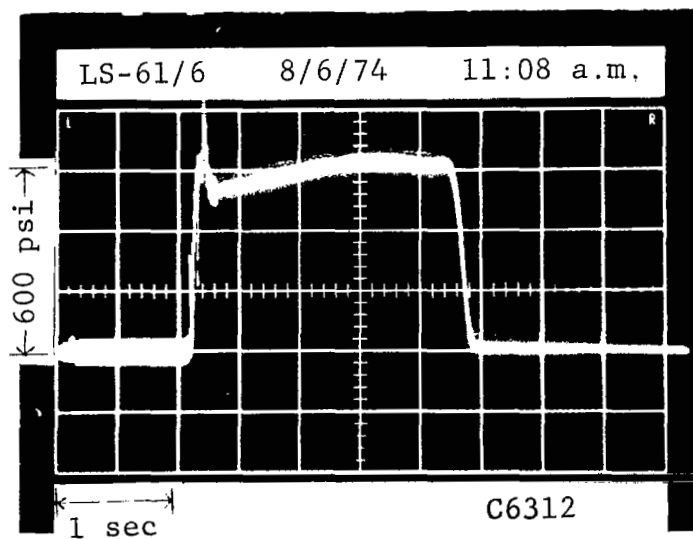
ROCKET MOTOR MOUNTING WITHIN 5.49 m (18 ft)
SPHERICAL CHAMBER

Photo taken after firing.
Note white Al_2O_3 dust on
upward facing surfaces.

Rocket housing diameter
is 7.5 cm (3 inches).



Test No. 3



Test No. 1

Figure 4

ROCKET FIRING PRESSURE TRACES

which occurred was about 225 on a mass basis. This is comparable to the dilution estimated by Hart (9) for the ground cloud from a Titan III launch before significant bouyant rise. Assuming that all the chlorine goes to HCl and all the aluminum goes to Al_2O_3 , the following initial concentrations in the chamber were expected,

HCl: 98.1 g, 1.134 g/m^3 , 772 ppm v/v*
 Al_2O_3 : 137.4 g, 1.588 g/m^3 , --

In the above concentrations, after-burning is considered to be complete. In some tests, further dilution of the exhaust cloud was performed by venting the chamber, as already described. This was done because the HCl and Al_2O_3 concentrations were high compared to the later stages of actual exhaust cloud development for which rainfall is a real possibility.

2.3 Rain Simulator

The raindrop generator was an important part of the scavenging tests. The function of the raindrop generator was to produce water drops of known size and fall velocity equal to the terminal velocity.

The raindrop generator used in the scavenging tests was based upon the capillary instability principle for making uniform sized drops. This method was selected over other devices, such as rain spray nozzles, because it provides control over both the drop diameter and its initial fall velocity. The theory of liquid jet breakup due to capillary instability was developed by Lord Rayleigh in 1878 (10). He showed that a laminar, low viscosity liquid jet is unstable due to surface tension, and tends to amplify longitudinal disturbances of a certain wavelength, λ , equal to 4.508 times the jet diameter, D_j . As the waves grow in amplitude, the jet breaks into equal sized segments. The

* Computed for 25°C , 745 mm Hg total pressure.

resulting drop diameter, D , is 1.89 times the jet diameter. In summary, the equations for Rayleigh breakup are:

$$\lambda = 4.508 D_j$$

$$D = 1.89 D_j$$

$$F = V_j / \lambda$$

where F is the applied perturbation frequency.

Literature subsequent to Rayleigh's work indicate that the generation of monodisperse droplets is achieved for λ/D_j in the range 3.5 to 7.0 (11,12,13,14). This result has been determined empirically. The optimum frequency calculated from the Rayleigh criteria is 1812 Hz for droplets near 1 mm in diameter. Droplets near this size are predicted by theory as the most prolific scavengers and therefore were selected as most appropriate for this work.

The raindrop generator was constructed by mounting a square-ended 20 gauge hypodermic needle mounted on a loudspeaker. An audio oscillator was used to perturb the liquid jet. Distilled water was introduced to the needle from a reservoir 1.5 m above. The distilled water flow rate was measured to be 0.791 ml/sec.

Experiments were performed with the raindrop generator to insure that drops of the predicted size were formed. The hypodermic needle was vibrated at various frequencies and the subsequent drop formation observed with a strobe light adjusted to a synchronous frequency. Results obtained at four vibration frequencies are shown in Table 1 where the generator is seen to function over a broad range of frequencies. Resonant frequencies of the hypodermic needle itself were avoided since characteristics of droplet formation were altered. The production of one drop per cycle of the driving oscillator was established with the strobe light.

Table 1

RESULTS OF RAINDROP GENERATOR TEST

<u>Needle Vibration Frequency, Hz</u>	<u>Highest Synchronous Strobe Freq., Hz</u>	<u>Drop Diameter, mm</u>		<u>Drop Spacing (mm)</u>	<u>Drop Velocity (cm/sec)</u>
		<u>Predicted</u>	<u>Observed</u>		
2,000	2,000	0.911	0.9	1.8	360
1,800	1,808	0.943	0.9	2.0	362
1,600	1,612	0.981	1.0	2.2	355
1,400	1,417	1.026	1.0	2.5	354

Test Conditions:

Water head = 1.5 m

Water flow rate = 0.791 ml/sec

Syringe needle: 20 g, square end

Observed liquid jet diameter without vibration = 0.5 mm

Theoretical frequencies for Rayleigh breakup:

maximum, 2,564 Hz; optimum, 1,812 Hz

The uniformity of droplet size with the Rayleigh breakup is evident from Figure 5. The exposure time for the photographs was $1/300$ sec. Hence, each drop image in the left photograph of Figure 5 is actually the superposition of $2000/300 \approx 7$ drops. The sharpness of the image shows that both the drop position and shape duplicate exactly from one drop to the next. From these and similar photographs, the drop diameter 5 cm below the hypodermic needle was measured. At a frequency of 1800 Hz for the constructed rain generator, the drop diameter measured was 0.9 mm. The measured drop velocity was 3.6 m/sec, which compares favorably to the terminal velocity for this size drop -- 3.65 m/sec (15).

Drops from the raindrop generator fall a distance of 2.8 m through the rocket exhaust cloud. Experiments were performed within the test chamber to further characterize the raindrops during their entire fall. Measurements were made throughout the entire rainfield to establish that the simulated rain was representative of naturally occurring rain.

It was observed that the water drop column spread laterally upon descent, probably due to interaction between drops or to small scale turbulence. The result was that the drops became randomly dispersed within a conical region. The full width of the cone is shown as a function of fall distance in Figure 6. At the location where the drops were collected, the drops fell within a circular area 23 cm in diameter. The random distribution of drops is seen in Figure 7. (Note that the drop images in Figure 7 vary in size, since the drops were not all in focus and were not uniformly illuminated.)

The observed lateral spreading of the drop stream insures that each drop passes through a chamber HCl concentration, not in the wake of a preceeding drop. The ratio of the drop

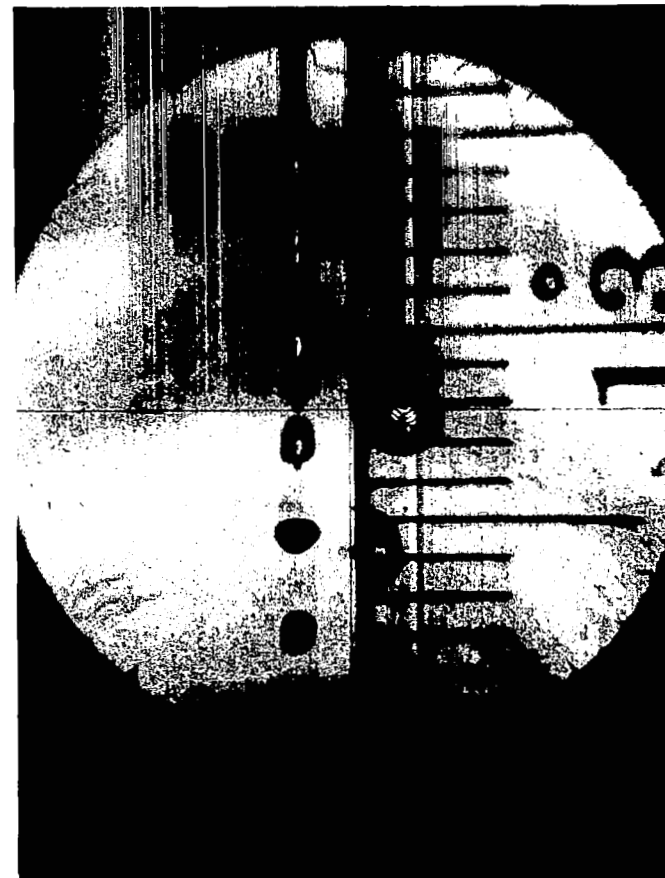
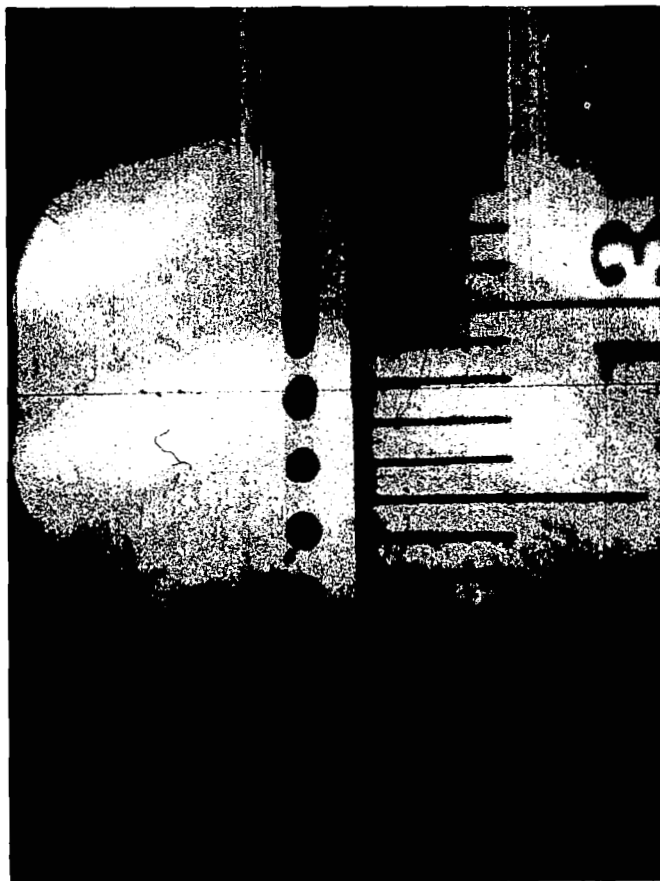


Figure 5

DROP GENERATOR IN RAYLEIGH BREAKUP MODE

Oscillator and Strobe light: 2,000 Hz (left), 1,400 Hz (right)
Distance from syringe needle: 5 cm
Photographic exposure time: 1/300 sec
A mm scale is shown in both photos

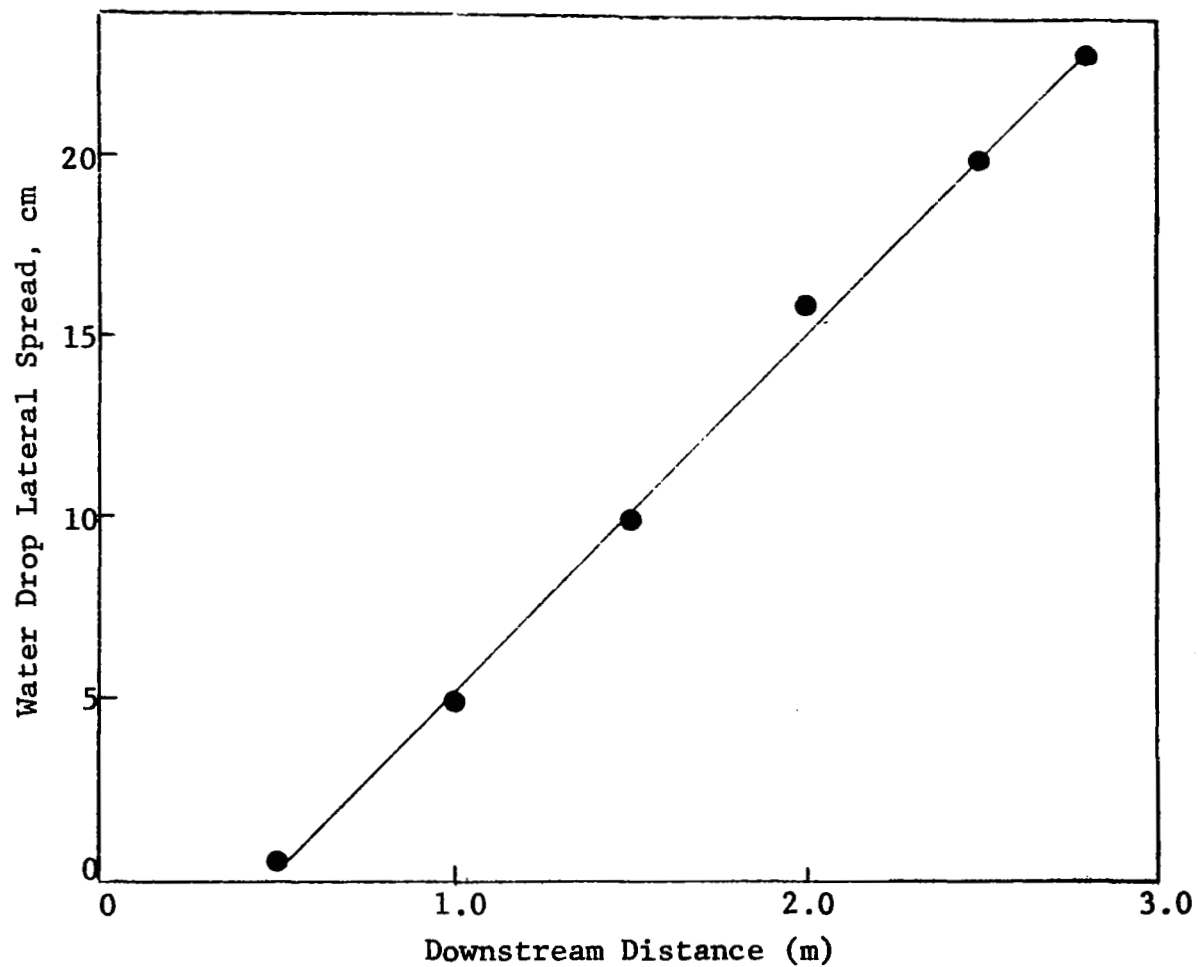


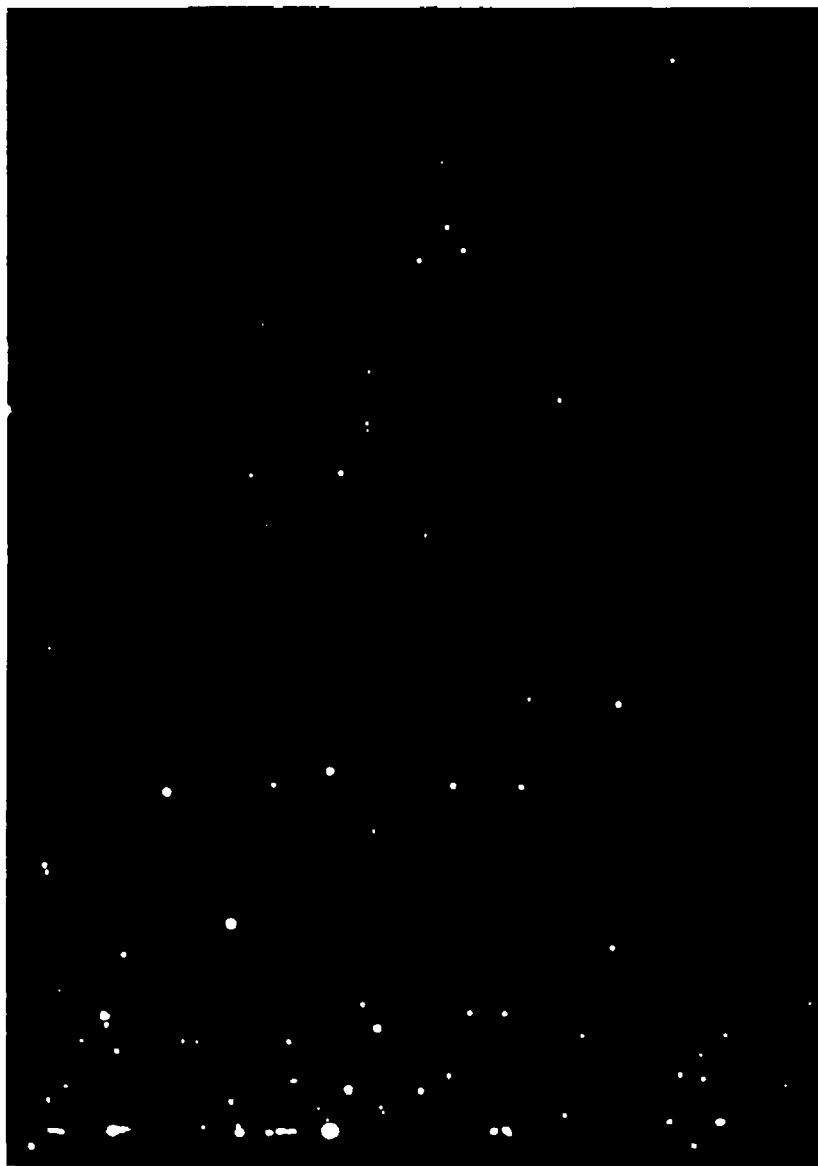
Figure 6

SPREADING OF RAINDROPS FROM RAIN SIMULATOR OVER ENTIRE LENGTH OF FALL

Cone volume = 0.15 m^3

Typical Cl^- content = 30 mg

Typical Cl^- catch by rain = 10 mg



←1 cm←

Figure 7

RAIN FIELD 2.7 m BELOW RAINDROP GENERATOR

Photo taken at $f/2.5$.
The variation in drop image
sizes is due to the limited
depth of field.

volume within the conical region to the volume of the region was computed to be 1.8×10^{-5} . The equivalent rainfall intensity at the location of the drop collector was approximately 5 mm/hr.

Droplet size was measured to be 0.9 mm near the nozzle exit. However, droplet size information at the location of collection is necessary to determine if droplet size is preserved during the fall. A double layer of oil was used to suspend the droplets collected. The specific gravity of the upper oil was less than one, while the lower oil specific gravity was greater than one*. In addition, the two oils used were immiscible in each other, and not soluble in water. A microscope with an optical scale was used to size the raindrops. The mean diameter of the raindrops was 0.89 mm, and the standard deviation was 0.21 mm. Hence, droplet size was preserved during the entire fall of 2.8 m. The frequency of the audio oscillator, which excited the raindrop simulator's transducer, was 1,800 Hz, which corresponds to the scavenging experiments.

2.4 Rain Collection and Reference Blank

During the rain scavenging experiment, the raindrops must be collected for purposes of analysis. This analysis yields information that permits calculation of a washout coefficient. Since contamination of the collected rain by the confined exhaust cloud was possible, precautions were taken.

A Pyrex pan (10 x 20 cm) was placed 2.8 m below the raindrop generator to collect the rain drops. The collection pan had a covering layer of silicone fluid** which reduced substantially the penetration of HCl from the exhaust cloud to

* Upper oil ~ heavy mineral oil
Lower oil ~ silicone fluid

** Dow Chemical Co., Midland, Michigan, #200 Silicone Fluid, 50 centistokes, 0.96 g/cc.

the rain water. The water drops were observed to penetrate the silicone fluid surface with a minimum of splashing. Thus, it is believed that the HCl absorbed in the drops remained with the drops. Within the fluid, the drops coalesced and fell to the bottom.

An identical Pyrex pan containing silicone fluid and water was used as a reference to permit correction for HCl penetration through the silicone fluid layer in the raindrop collector.

For rocket tests 9, 10, and 11, Pyrex funnels, circular in cross-section with a stopcock, were used for rain collection and as a reference. In this way, the desired samples were withdrawn from below the layer of silicone fluid rather than simply pouring as with the Pyrex pans. With this technique, the possibility of acid mist droplets existing on the upper surface of the silicone layer contaminating the water sample was removed.

The HCl catch in the rain sample was corrected for HCl absorption after raindrop fall as follows: since the rain collection and reference water pans or funnels had identical dimensions and amount of silicone fluid, the HCl penetration through the silicone fluid was assumed equal for both. Hence, the Cl^- content of the reference sample was subtracted from the Cl^- content of the rain sample. A chloride-specific ion electrode was employed to measure the Cl^- content in the samples. Results of the scavenging tests are given in Section 4 of this report.

2.5 Hydrogen Chloride Concentration

Measurement of the rocket exhaust cloud HCl concentration was performed with bubblers. Distilled water was used as the absorbing fluid for all the tests. The bubblers were located inside the test chamber to eliminate sampling line losses. After removal of the bubblers from the chamber, all components were rinsed thoroughly with distilled water to retrieve all the HCl.

The bubblers were always used in tandem -- the second bubbler serving as backup to the first. The HCl catch in the first bubbler was 75-90% of the total combined catch. An additional bubbler was used as a reference and was located inside the chamber for the duration of the test. The reference bubbler remained unused over the entire test period. The purpose of the reference bubbler was to correct for HCl absorption while the bubbler was idle. Correction was made by subtraction of the reference sample HCl content. All bubblers were introduced and removed from the chamber simultaneously. A chloride-specific ion electrode was used to determine the Cl^- content of all samples. In most cases, pH measurements were also made.

Mass balance considerations reported in Appendix B of this report show that the chamber HCl concentration as measured by the bubblers, together with the measured HCl deposition on the chamber walls, accounts for from 82 to 94% of the theoretical HCl. This indicates that the bubbler measurement of total airborne HCl is essentially sound.

In each test, measurements were also made of the chamber pressure and temperature histories and the Al_2O_3 particle concentration and size distribution. Since these measurements are not essential to the scavenging experiment, discussion is reserved for Appendix A.

3. EXPERIMENTAL PROCEDURE

This section describes the manner in which the rocket exhaust cloud rain scavenging experiments were conducted. A chronological history of a typical rocket test follows:

1. Spherical test chamber was conditioned to the desired relative humidity. This was accomplished by wetting the inside chamber walls and allowing equilibration to take place. Prior to rocket ignition, the test chamber was vented to the desired relative humidity.
2. Instrumentation was installed and any special experiments are conducted or set up.
3. The test chamber was completely sealed and the rocket is ignited thus generating the exhaust cloud. The thermodynamic properties vary substantially over a ten minute period after rocket ignition.
4. In those tests where venting was employed to reduce the HCl concentration, venting was initiated after the chamber pressure had returned to ambient. After a predetermined period of venting, the chamber was resealed.
5. The first chamber HCl concentration measurement via bubbler was initiated. Three consecutive 20 minutes bubbler samples were taken in each test.
6. The raindrop scavenging experiment was sequenced so as to coincide with the midpoint of operation of the desired bubbler sample. The Al_2O_3 particle sample was taken simultaneously with the scavenging experiment. Thus the scavenging, HCl, and Al_2O_3 data were obtained concurrently.
7. For the duration of the test, condensation nuclei counts, pressure, and temperature were monitored.
8. The test chamber was opened ($1\frac{1}{2}$ hours after rocket ignition typically) and vented for at least one hour. Instrumentation was removed and any special experiments were concluded. Samples were retrieved and stored in a stable manner.

4. EXPERIMENTAL RESULTS

The main results in these experiments consist of the scavenging data for 0.9 mm water drops falling at terminal velocity. These results are discussed in the present section. Ancillary experiments were done simultaneously to establish the mass balance for HCl and to determine the HCl absorption characteristics of various surfaces. The mass balance results are discussed in Appendices A and B, while the absorption results are discussed in Appendix C.

The results of scavenging tests 1 through 5 were reported in detail in a previous report (7). For completeness, however, the key data from test 1 through 5 will be included here along with the data from the more recent tests.

4.1 Test Conditions

The test conditions for scavenging tests 1 through 11 are given in Table 2. It is noted that the humidity range covered by the scavenging tests is 54 to 98% RH. The humidity cited in Table 2 includes the water of combustion and the effects of venting, if used. The reference temperature for the relative humidity is the chamber pre-firing dry bulb temperature.

As seen in Table 2, partial venting of the chamber was done prior to the scavenging experiment in tests 9, 10, and 11.

4.2 Scavenging Test Results

The scavenging tests were performed using the apparatus described in Section 2 and the procedure described in Section 3. The key results are shown in Table 3.

The scavenging data obtained in test 3-8, 10, and 11 are considered satisfactory. Reliable data were not obtained in tests 1 and 9, due to the very small amount of rain caught. Test 2 did not provide reliable data, due to a difficulty in the bubbler measurement of the chamber HCl concentration.

Table 2

TEST CONDITIONS FOR SCAVENGING TESTS

Test Number	Test Date	Chamber Pre-Firing Conditions				Initial Venting Period, min.	Post-Firing/Venting	
		Baro. Press. mm Hg	Dry Bulb, °C	Wet Bulb, °C	Rel. Hum., %		Rel.* Hum., %	Acid** Droplets Expected?
1	02/04/74	752.8	17.2	-	~20	0	-	No
2	02/14/74	748.6	17.2	10.5	41	0	54	No
3	02/27/74	745.3	17.8	41.1	66	0	77	No
4	03/15/74	747.5	20.0	15.0	59	0	69	No
5	03/28/74	746.1	18.5	15.5	72	0	83	Yes
6	06/06/74	741.3	23.3	19.5	69	0	75	No
7	06/13/74	747.8	24.0	23.0	92	0	98	Yes
8	06/26/74	751.1	25.0	22.5	81	0	87	Yes
9	08/06/74	755.0	21.5	20.0	87	5	83	Yes
10	08/16/74	749.5	25.0	24.0	70	15	70	No
11	09/26/74	742.5	23.0	22.0	71	15	71	No

* Expresses total water content at stated dry bulb temperature. Water of combustion and effect of venting included.

** The criterion adopted is 81% RH, regardless of HCl concentration.

Table 3

RESULTS OF THE SCAVENGING TESTS

Test Number	Rain Sample		Reference Sample		Net Collection by Rain		Chamber HCl Concentration*	
	Volume, ml	mg Cl ⁻	Volume, ml	mg Cl ⁻	Net mg Cl ⁻	mg Cl ⁻ per l	g Cl ⁻ per m ³	ppm
1	8	-	-	0.43	-	-		
2	88	62	-	1.1	61	692		
3	308	88	-	10.0	78	253	0.369	250
4	152	27.7	170	10.0	17.7	116	0.259	175
5	121	24.2	118	4.1	20.1	166	0.222	150
6	133	11.4	224	1.7	9.7	72.9	0.114	80
7	138	37.3	210	15.9	21.4	155	0.346	200
8	61	11.8	202	7.1	4.6	75.4	0.100	100
9	3	-	102	6.5	-	-	0.170	211
10	69	2.6	106	1.9	0.7	10.1	0.035	24.5
11	84	4.2	102	2.6	1.6	19.4	0.255	159

* As measured by a bubbler operated at the time of the scavenging test.

The calculations reported in Table 3 are based on the chloride ion measurements exclusively. Since chlorides are common substances, there is a possibility of high readings due to contamination. As a check, the pH was also measured for most of the rain samples, reference samples, and bubbler samples. The pH measurements generally corroborated the chloride ion measurements. The average of the difference $\text{pH}-\text{pCl}$ was less than 0.01 for each of the three classes of samples.

The scavenging data from Table 3 are plotted in Figure 8. One adjustment was made in plotting the data: the measured chamber HCl concentration in test 11 was replaced by the value obtained in test 10. This step was taken because the measured value in test 11 is incongruous with other data. The high measured HCl concentration in test 11 is at variance with the low measured concentration of Al_2O_3 particles (see Appendix A), as well as with the low value obtained in the rain reference sample. Since tests 10 and 11 were done under identical conditions, the HCl concentration obtained in test 10 was used for both tests in plotting Figure 8.

The experimental points in Figure 8 lie along a line of unit slope in the log-log plot. This shows that the HCl picked up by the 0.9 mm drops in falling 2.8 m at terminal velocity is proportional to the chamber HCl concentration, as measured by bubbler. This is an important result, since it shows that scavenging is a linear process.

Also shown in Figure 8 is one calculated curve. The heavy upper line is calculated from the standard Frossling correlation (16) for absorption of a soluble gas by a moving liquid drop. The diffusion coefficient of HCl required in applying Frossling's correlation was estimated by the technique recommended in the Chemical Engineers Handbook (17). The value obtained was $0.173 \text{ cm}^2/\text{sec}$. It is seen that the present data are below Frossling's correlation by a factor of 2.

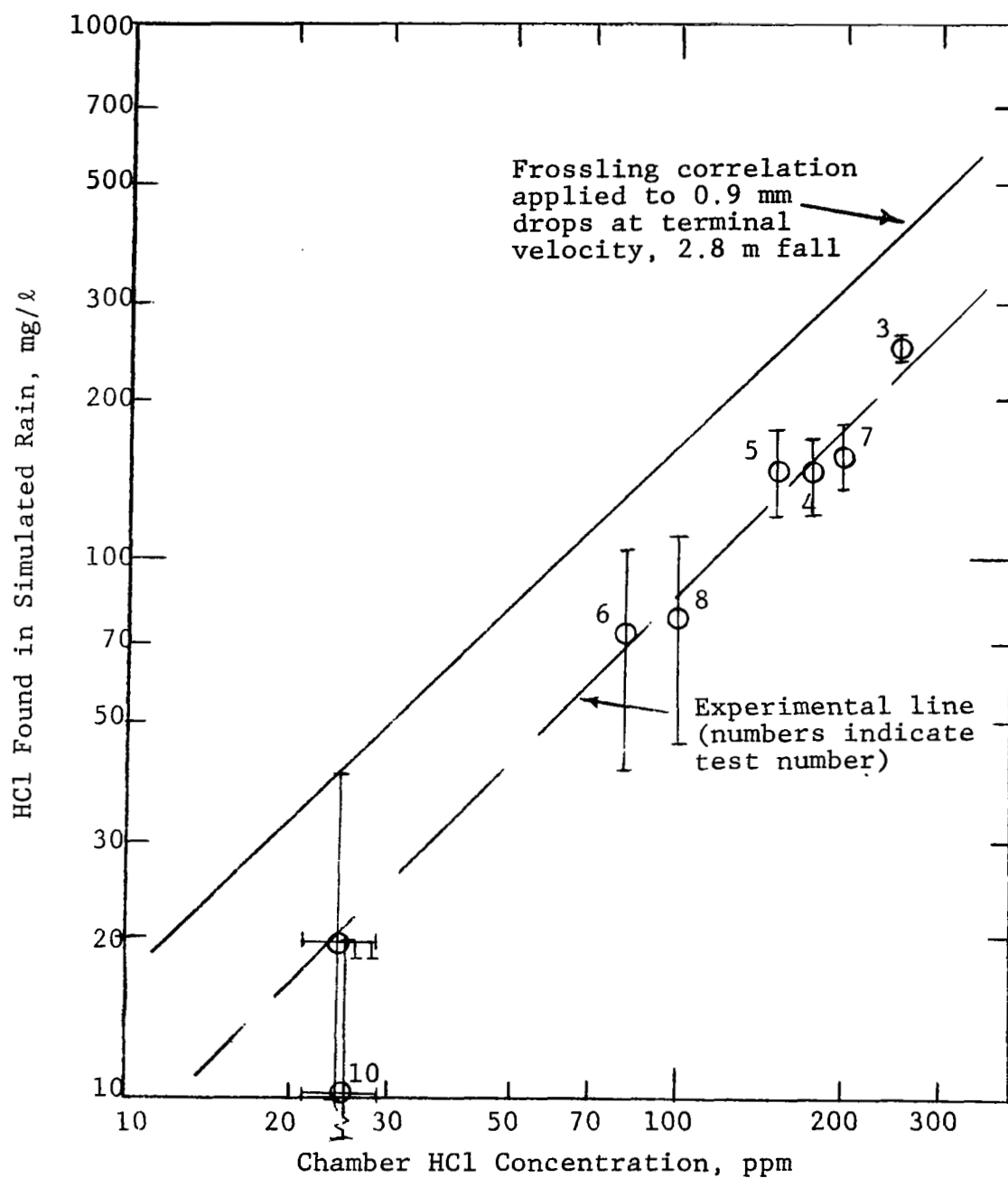


Figure 8
EXPERIMENTAL SCAVENGING RESULTS

The data points plotted in Figure 8 cover a humidity range of 69 to 98% RH. The humidity is seen to have virtually no effect on the scavenging process. The lack of an effect was surprising, since acid droplet formation was expected to occur at some point within this humidity range. Such droplets would absorb a large fraction of the total HCl. Thus, at suitably high humidity, the HCl removal mechanism was expected to change from gas scavenging to scavenging of droplets. This fundamental change in scavenging mechanism should be reflected by a significant change in the Cl^- pickup by the drop. The observed lack of a humidity effect suggests that the expected acid droplet formation did not occur in these tests.

The results of the scavenging experiments may be stated as follows: the pickup of HCl by water drops falling at their terminal velocity is 0.5 times the value predicted by the Frossling correlation. Although this statement is based on experiments conducted with 0.9 mm diameter drops exclusively, we anticipate that the rule will hold for other sizes as well. The dependence of scavenging on drop size should be checked in future tests.

The error bars shown in Figure 8 were estimated from the data on the rain blanks in tests 1 through 8. Since these blanks were exposed to nearly identical exhaust cloud conditions, the variations among the measured HCl contents is an indication of the uncertainties in the experiment.

5. EXTENSION TO SCAVENGING BY A POST-LAUNCH RAIN

The scavenging of HCl from a rocket exhaust cloud may be calculated from the experimental results just described, together with information on the spectrum of raindrop sizes and the fall velocity of raindrops as a function of size. This calculation has been carried out and the results are reported in this section.

The expression for raindrop concentration and size used in this work was that of Marshall and Palmer (18). The expression is:

$$C_{rd} = 0.08 \exp (-41D/R^{0.21})$$

where

C_{rd} = the concentration of raindrops of diameter D to D+dD, in drops/cc/cm

D = the raindrop diameter, in cm

R = the rainfall intensity, in mm/hr

The Marshall-Palmer expression was checked against observed raindrop size spectra by Dingle and Hardy (19). They concluded that the expression fit well enough on the average, although considerable differences were observed for some individual rainfalls.

Gunn and Kinzer's (15) data were used for the fall velocity of raindrops. These data were used directly in the tabular form given by the authors. Their data are reproduced here in Table 4. These data were assumed to apply throughout the temperature and humidity range of interest.

The rate of HCl absorption by a single drop was computed from a chemical engineering mass transfer expression (16,20), modified per the results of the chamber scavenging tests.

Table 4

GUNN-KINZER DATA ON RAINDROP FALL VELOCITY
(From Ref. 15)

<u>Drop Diameter, cm</u>	<u>Terminal Velocity, cm/sec.</u>
0.02	72
0.04	162
0.06	247
0.08	327
0.10	403
0.12	464
0.14	517
0.16	565
0.18	609
0.20	649
0.22	690
0.24	727
0.26	757
0.28	782
0.30	806
0.32	826
0.34	844
0.36	860
0.38	872
0.40	883
0.42	892
0.44	898
0.46	903
0.48	907
0.50	909
0.52	912
0.54	914
0.56	916
0.58	917

The expression is*

$$R_A(D) = k_y \pi D^2 M_A$$

where

$R_A(D)$ = the rate of HCl absorption by a single drop of diameter D , in g/sec

$k_y = D_A/D \text{ Sh}$, is the mass transfer coefficient, cm/sec

D_A = the diffusion coefficient of HCl in air, cm²/sec

Sh = the Sherwood number

$$= 0.5 (2 + 0.6 \sqrt{\text{Re}} (\text{Sc})^{1/3})$$

(the factor 0.5 was prefixed to the standard Frossling correlation, as suggested from the experiments)

M_A = the mass concentration of HCl in the cloud, g/m³

$\text{Re} = DV_s/\nu$, the Reynolds number

$\text{Sc} = \nu/D_A$, the Schmidt number

ν = the kinematic viscosity of air, in cm²/sec

D = the raindrop diameter, cm

V_s = the raindrop fall velocity, in cm/sec

Note that the standard Frossling correlation has been modified by prefixing a factor 0.5.

The diffusion coefficient, D_A , was estimated by a procedure recommended in the Chemical Engineer's Handbook (17). The result obtained for 15°C and 1 atm was 0.1730 cm²/sec. This value was used for all temperatures considered.

The kinematic viscosity of air was computed from the expression

* The desorption term included by Hales (20) was not included here; the high solubility of HCl in water makes the desorption term unnecessary.

$$v = 0.1177 (T/273.2)^{1.79}, \text{ in cm}^2/\text{sec}$$

where was obtained by fitting an equation to data tabulated by Eckert and Drake (21). The value 0.755 was used for the Schmidt number.

The rate of removal, R , of HCl from a cubic meter of the exhaust cloud was then calculated by integrating the single-drop removal rate over the raindrop size spectrum.

$$R = \int R_A(D) C_{rd}(D) dD$$

The washout coefficient, Λ , is defined as the rate of removal divided by the HCl concentration. Thus

$$\Lambda = \frac{1}{M_A} \int R_A(D) C_{rd}(D) dD = \int k_y \pi D^2 C_{rd}(D) dD$$

It is noted that this washout model is linear, since the washout coefficient, Λ , is independent of the concentration, M_A . This linearity is an important feature in applications.

The expression for the washout coefficient was integrated numerically (Simpson's rule, panel size $\Delta D = 0.04$ cm) for several rainfall intensities from 1 to 30 mm/hr. The results of these integrations can be expressed accurately by the compact formula

$$\Lambda = 8.3 \times 10^{-5} R^{0.567}$$

where Λ is in sec^{-1} and the rainfall intensity, R , is in mm/hr.

6. EXAMPLE APPLICATION: HYPOTHETICAL TITAN LAUNCH AT KENNEDY SPACE CENTER

In this section, the washout expression presented at the conclusion of the preceeding section is applied to estimate the precipitation scavenging of HCl following a Titan IIIC launch at Kennedy Space Center. Sea breeze meteorological conditions are assumed. A standard KSC rain cycle, with periods of light, medium, and heavy rain, is assumed to start 30 minutes after launch. This example makes use of documented exhaust cloud dynamics and rain data.

The cloud dynamics used in this example are taken from Dumbauld, et al (22). The assumed fuel load* was 40,815 kg. Under the meteorological conditions assumed, the cloud stabilization height was calculated to be 800 m (cloud center).

An idealized rain cycle (23) was adopted, with certain modifications, to describe the assumed post-launch rain. The cycle, as given in the reference, was presented as a model of an extreme-case (95th percentile) heavy rain at Kennedy Space Center. This is not appropriate as a model for a post-launch rain, since launch operations would probably not be conducted if an extreme-case heavy rain were imminent. The idealized rain cycle was therefore modified to describe a typical, or median, rain. This was done with the aid of Table 4.12 of Reference 23. The resulting rain cycle is given in Table 5.

It has been shown (24) that the effect of a linear, time- and space-independent, washout process on a pollutant cloud is to reduce the pollutant concentration at all points within the cloud by the factor $\exp(-\Lambda t)$, where Λ is the washout coefficient and t is time since onset of rain. The effect of several periods, t_1, t_2, \dots , of rain at different intensities, $\Lambda_1, \Lambda_2, \dots$, is given by $\exp(-\Lambda_1 t_1 - \Lambda_2 t_2 - \dots)$. Thus, the effect of the idealized rain cycle on a solid rocket exhaust cloud may be computed without detailed knowledge

*effective for assumptions

Table 5

IDEALIZED MODEL OF A POST-LAUNCH RAIN

50th percentile rainfall intensities are used.

<u>Time Period, min*</u>	<u>Rain Intensity, mm/hr</u>
0 - 60	6.4 "light rain"
60 - 65	66.0 "heavy rain"
65 - 80	24.0 "medium rain"
80 - 140	6.4 "light rain"

* Origin of time scale arbitrary.

of the cloud location, size, or concentration. The results of this calculation are given in Table 6. The reduction factors are to be applied in addition to the cloud concentration decrease due to dispersion.

The reduction factors given in Table 6 were applied to the cloud center concentrations from Reference 22. The results are shown in Figure 9. The rain cycle was assumed to start 15 minutes after launch.

Figure 9 shows that the effect of rain scavenging on the cloud concentration at its centroid is slight during the first rain cycle segment (60 min of light rain), but is more pronounced during the periods of heavy and medium rain. The second period of light rain has an apparently larger relative effect. This is due to the fact that, in the absence of rain, the cloud centroid concentration decreases at a rate proportional to time^{-1} , while the effect of scavenging is to reduce the concentration according to the exponential factor $e^{-\Lambda t}$.

Table 6

REDUCTION OF HCl CONCENTRATION IN A SOLID ROCKET EXHAUST CLOUD DUE TO THE IDEALIZED POST-LAUNCH RAIN CYCLE

Rain Cycle Period, min	Rain Intensity, mm/hr	Washout Coefficient, Λ		Cumulative Reduction of Concentration
		in sec^{-1}	in $\% \text{ min}^{-1}$	
0-60	6.4	0.000238	1.4	0.350
60-65	66.0	0.000893	5.4	0.504
65-80	24.0	0.000304	1.8	0.684
80-140	6.4	0.000238	1.4	0.794

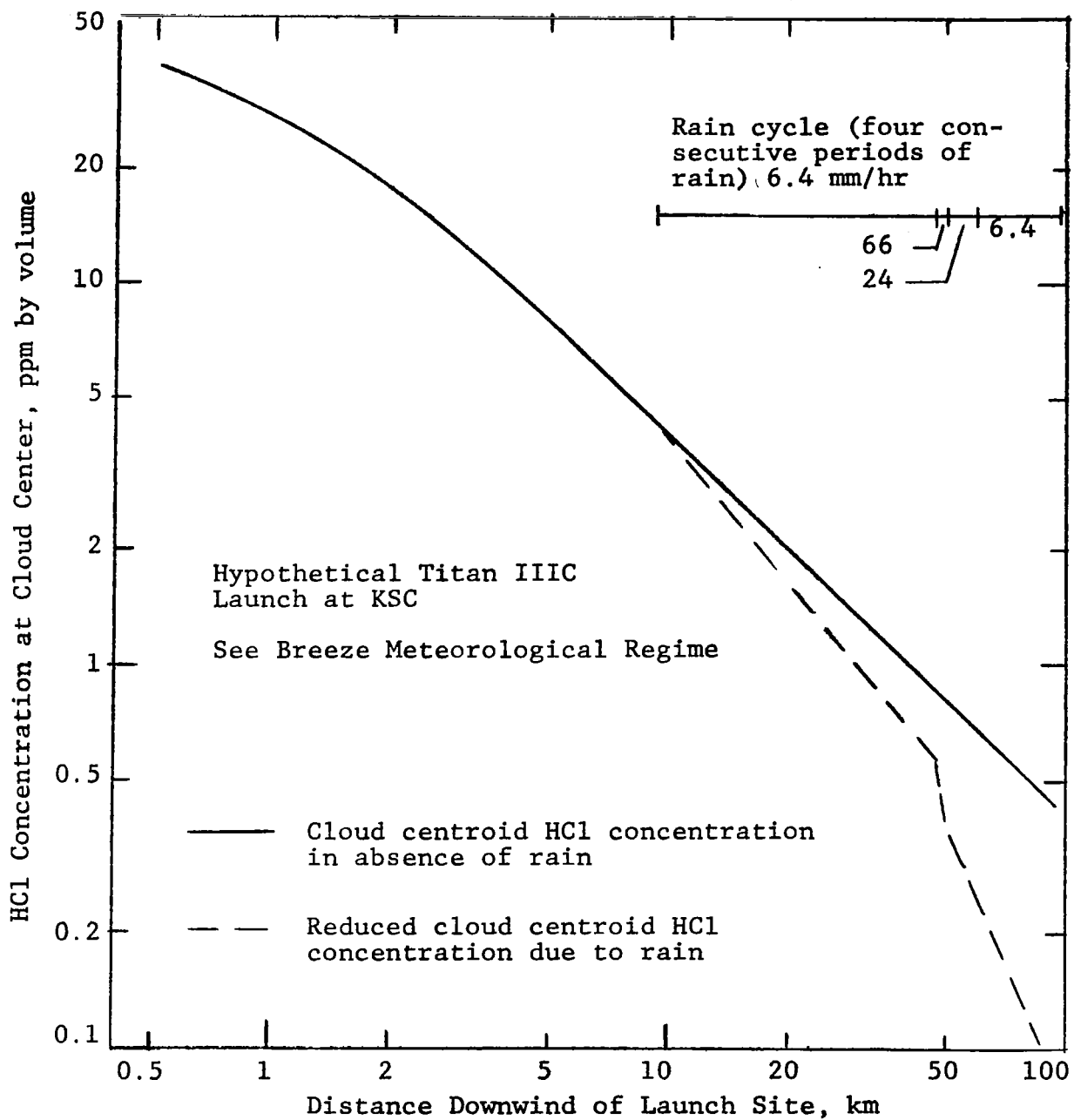


Figure 9

EFFECT OF SCAVENGING UPON EXHAUST CLOUD CENTROID CONCENTRATION

7. CONCLUSIONS

Eight scavenging tests were conducted using the confined exhaust cloud from a 0.454 kg solid rocket motor. In these tests, direct measurement was made of the HCl acquired by 0.9 mm water drops falling 2.8 m through the exhaust cloud at terminal velocity. The chamber HCl concentration at the time of the scavenging experiment was measured in each test by means of bubblers.

The tests showed that the HCl acquisition by falling water drops is directly proportional to the HCl concentration in the cloud, and is virtually unaffected by humidity variations in the range 69 to 98%. A line fit to the data points was parallel to the line predicted by the classical Frössling correlation for the absorption of a soluble gas by a moving water drop. The experimental line, however, was lower than the Frössling correlation by a factor of approximately 2.

In work at Langley Research Center, Pellett (7) also determined the HCl absorption by falling water drops. Pellett employed laboratory-scale apparatus, permitting close control over the experimental variables. The drops were not at terminal velocity and the scavenging cell contained a dry, particle-free HCl-N₂ mixture. Pellett's results fit the Frössling correlation. It is not known if the factor-of-2 difference between Pellett's results and those reported here is due to the influence of exhaust cloud particles or to differences in the experimental approach.

Measurements of the HCl deposition on the chamber walls were made in two tests. The measured chamber HCl concentration, together with the measured HCl deposition on the walls, accounted for 81 to 94% of the theoretical HCl in the two tests. This demonstrates that the bubbler method of measuring chamber HCl concentration was adequate for the conditions encountered in the tests.

The experimental scavenging results for 0.9 mm water drops were extended to the entire spectrum of raindrop sizes using the empirically-adjusted Frössling correlation and the Marshall-Palmer expression for the raindrop size spectrum. The result was a compact expression for the washout coefficient, Λ . The expression is:

$$\Lambda = 8.3 \times 10^{-5} R^{0.567}$$

where Λ is in sec^{-1} and R is the rainfall intensity in mm/hr. A comparable expression,

$$\Lambda = 1.11 \times 10^{-4} R^{0.625}$$

was derived by Pellett (7), based on his measurements of HCl scavenging. The difference between the two expressions is due largely to the factor-of-2 difference in the measured scavenging efficiency for a single drop size.

The empirical expression for the washout coefficient was applied to a hypothetical solid rocket launch at Kennedy Space Center under sea breeze meteorological conditions. An idealized rain cycle, including periods of light, medium, and heavy rain, was adopted to represent a post-launch rain. This example showed that light rain occurring shortly after the launch, when the normal dilution rate due to atmospheric mixing is high, has a relatively slight effect on the cloud HCl concentration. The relative effect became significant, however, at higher rain intensities and at later stages of the cloud history.

The most significant result of these tests was that scavenging of HCl from a solid rocket exhaust cloud is not affected by the Al_2O_3 particles and water vapor in the cloud to the extent anticipated. A potential factor-of-10 reduction was anticipated, based on comparing Kerker and Hampl's (6) results for scavenging of particles to Pellett's (7) results for HCl gas scavenging (see Section 1). The present tests

showed that the reduction of HCl scavenging due to other exhaust cloud constituents does not exceed a factor of 2.

8. RECOMMENDATIONS

It is recommended that the expression

$$\Lambda = 8.3 \times 10^{-5} R^{0.567}$$

be used to predict washout of HCl from rocket exhaust clouds by rain. In this expression, Λ is the washout coefficient in sec^{-1} and R is the rain intensity in mm/hr.

Further work is recommended to test the above expression over a wider range of experimental conditions. Specific recommendations are:

1. Experiments should be run for drop sizes other than the 0.9 mm used in this work. At the same time, the drop generator should be modified to better simulate rain.
2. Experiments should be run at lower exhaust cloud concentrations. HCl concentrations in the range 5-25 ppm should be used. This requires a general upgrading of the measurement techniques.
3. Future experiments should include instrumentation to directly measure HCl acid droplets formed in the exhaust cloud, and thereby determine the partition of cloud HCl between the gas and liquid phases.

Recommendation 3 is motivated by the fact that the anticipated humidity effect on scavenging was not observed in the present experiments. This indicates a serious gap in our knowledge of the microphysics and microchemistry of solid rocket exhaust clouds. Data on HCl gas/liquid partitioning would be a major step towards closing this gap.

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Appendix A

TEMPERATURE, PRESSURE, HCl, AND Al_2O_3 HISTORY FOR
THE CONFINED ROCKET EXHAUST CLOUD

TEMPERATURE, PRESSURE, HCl, AND Al₂O₃ HISTORY FOR THE CONFINED ROCKET EXHAUST CLOUD

1. INTRODUCTION

It was observed repeatedly in the course of the experimental work that the measured HCl concentration in the chamber after rocket firing was substantially less than that expected on the basis of the solid rocket fuel composition. This observation prompted an investigation of the initial values and decay rates for temperature, pressure, HCl concentration, and Al₂O₃ concentration for the rocket exhaust cloud. The results are reported in this Appendix.

2. EXPECTED INITIAL EXHAUST CLOUD PARAMETERS

The fuel for the solid rockets used in these experiments consisted of 318 g of ammonium perchlorate, 72.6 g of aluminum powder, and 63.6 g of PBAN binder (A1). The combustion thermochemistry of this fuel has been documented (A2,A3,A4,A5,A6). The exhaust products and energy release are listed in Table A1. Complete afterburning of H₂ and CO appears to be established (A2,A4,A6) and is assumed in Table A1.

The expected initial exhaust product concentrations and the expected temperature and pressure rise are shown in Table A2. It is assumed that the exhaust products and heat energy mix thoroughly with the chamber air within 15-30 seconds after firing. Losses to the chamber walls during that time period are not taken into account in Table A2.

3. EXPECTED RATES OF DECAY OF EXHAUST CLOUD PARAMETERS

Several of the exhaust cloud constituents are expected to decrease during the period after the rocket firing by transfer processes to the chamber walls. For example, the chamber walls form a heat sink with capacity ~ 5000 kcal/°C. Thus, the chamber walls are capable of absorbing the full heat of combustion, resulting in a wall temperature rise of only ~ 0.25°C. Similarly, HCl could be absorbed by the paint

Table A1

ROCKET EXHAUST PRODUCTS AND HEAT RELEASE

Rocket Propellant Composition (A1,A2)

Ammonium perchlorate (70%)		317.8 g
N	37.8 g	
H	10.8 g	
Cl	96.0 g	
O	173.1 g	
Aluminum (16%)		72.6 g
PBAN (14%)		63.6 g
C	49.6 g	
H	5.74 g	
O	6.39 g	
N	1.94 g	
Total		<u>454 g</u>

Exhaust Products (complete afterburning is assumed, so that all H goes to H₂O, and all C goes to CO₂)

HCl	98.0 g	2.68 moles
Al ₂ O ₃	137.3 g	-
CO ₂	188.0 g	4.27 moles
H ₂ O	152.1 g	8.45 moles
N ₂	39.5 g	1.41 moles
Total	<u>614.9 g</u>	<u>16.81 moles gas</u>
Chamber O ₂ consumed in afterburning	160.9 g	5.03 moles
Net exhaust products	454 g	11.78 moles gas

Heat Release (A3)

From primary combustion (1.41 kcal/g)	640 kcal
From afterburning (1.37 kcal/g)	622 kcal
Total	<u>1262 kcal</u>
Possible additional heat release by formation of 20 wt % HCl acid (105.2 kcal/mole HCl)	282 kcal

Table A2

EXPECTED POST-FIRING CHAMBER CONDITIONS

Chamber Volume and Pre-Firing Air Content

Shape	sphere
Diameter	5.49 m ₃
Volume	86.47 m ³
Surface	94.69 m ²
Typical pre-firing conditions	
Temperature	25°C
Absolute pressure	746 mm Hg
Gas content (H ₂ O vapor included)	3472 moles
H ₂ O vapor content	up to 110 moles

Expected Post-Firing Conditions

HCl (772 ppm)	1.13 g/m ³
Al ₂ O ₃	1.55 g/m ³
Moles gas added (assuming no condensation)	11.78 moles
Maximum temperature increase (specific heat at constant volume = 5 cal/mole)	72°C
Maximum pressure rise (from ideal gas law)	141 mm Hg

on the wall, with or without chemical reaction. The presence of a moisture film would ensure a large capacity of HCl absorption: a film thickness of only 5 μm corresponds to 500 ml of water, sufficient to absorb all the HCl. Finally, the deposition of Al_2O_3 particles on the wall is limited only by the sedimentation and diffusional velocity of the particles.

The absolute rates of heat and mass transfer to the wall are difficult to predict. This is particularly true in the first 15-30 seconds after firing, when strong air motion is observable in the chamber. The heat transfer during this time includes radiation heat transfer from the rocket flame lance and adiabatic cooling due to gas escape through chamber leaks. It is clear, however, that the initial 15-30 second period involves relatively high heat and mass transfer rates.

By 60 seconds after firing, the chamber air velocities are greatly reduced. A mild stirring persists through the test period, however, driven initially by thermal gradients (bouyancy forces). During this period, heat transfer occurs primarily by the free convection mechanism. Unfortunately, handbook values of the heat transfer do not cover the case of a free convection, interior flow required for this case.

Although prediction of the absolute rates of decay of the exhaust cloud parameters appears out of reach, definite rules exist which govern the relative rates of decay. For example, in the absence of chamber leaks and changes of phase, the absolute pressure and temperature must decay at the same rate, since they are coupled by the ideal gas law. The same applies to the chamber excess temperature and pressure. Chamber leakage would modify this relationship: leakage is equivalent to an adiabatic expansion, for which the absolute temperature decreases with the 0.286 power of the absolute pressure. Furthermore, calculations show that condensation, whether in the chamber volume (droplet formation) or on the walls, would have very little effect on the relative rates of

decrease of temperature and pressure. The absolute rates of both, however, could be affected by droplet formation. Onset of droplet formation would produce a break in the slope of both the cooling curve and the pressure decay curve at the dew point temperature.

Two possibilities are foreseen with regard to the rate of decrease of HCl relative to that of temperature. If the chamber HCl remains in the gas phase and if the capacity of the wall to absorb HCl is sufficient, the relative rates of decay of HCl and temperature will be governed by the analogy between heat and mass transfer. According to this principle, the Sherwood number for mass transfer for this case is numerically equal to the Nusselt number of heat transfer (A7). Consequently, the rates of decay of HCl and excess temperature are in the ratio of their diffusivities ($0.173 \text{ cm}^2/\text{sec}$ for HCl and $0.300 \text{ cm}^2/\text{sec}$ for heat). Thus, the rate of HCl loss should be 0.58 times the rate of temperature decay.

Conversely, if all or part of the chamber HCl absorbs on particles or is involved in droplet formation, its decay rate is expected to be quite different from that of temperature. Droplets of particles of diameter less than $0.1 \text{ }\mu\text{m}$ deposit on chamber walls primarily by diffusion (Brownian motion). Particles larger than $1.0 \text{ }\mu\text{m}$ deposit primarily by sedimentation. Sedimentation in a chamber with mild stirring was discussed by Fuchs (A8). The process leads to an exponential decay of concentration, at a rate that is strongly dependent on particle size. The estimated deposition rates for the present chamber are given in Table A3.

The rate of loss of Al_2O_3 particles is governed by the mechanisms just discussed for droplets. The loss rates are shown in Table A3. The loss rates are larger than for water drops due to the difference in density. If condensation occurs upon the Al_2O_3 particles, the loss rates would be intermediate to those given.

Table A3

EXPECTED RATES OF DECREASE OF EXHAUST CLOUD PARAMETERS

Temperature vs. Pressure.

In the absence of condensation or substantial chamber leaks, temperature and pressure should decay at the same rate. Condensation has little effect on the relative rates, but affects the absolute rates. Chamber leaks enhance the pressure decay relative to the temperature decay.

HCl vs. Temperature.

If the HCl remains in gas phase and the chamber wall capacity for HCl absorption is large, HCl will decay at 0.58 times the rate of temperature decay.

Decrease of Droplet or Al_2O_3 Particle Concentration

<u>Particle Size, μm</u>	<u>Rate of Decrease, % min^{-1}</u>	
	<u>Droplets</u>	<u>Al_2O_3 Particles</u>
0.5	0.014	0.056
0.7	0.026	0.102
1.0	0.049	0.197
1.5	0.111	0.443
2.0	0.197	0.787
3.0	0.442	1.77
5.0	1.23	4.92
7.0	2.41	9.64
10.0	4.92	19.7
15.0	11.1	44.3

4. MEASURED EXHAUST CLOUD PARAMETERS

Four exhaust cloud parameters were monitored during the tests. These were:

1. Chamber pressure
2. Exhaust cloud temperature
3. Exhaust cloud HCl content
4. Exhaust cloud Al_2O_3 particle mass concentration

In addition, certain direct measurements were made on the HCl and Al_2O_3 deposition on the chamber walls. These measurements are discussed below.

4.1 Chamber Pressure and Temperature

The chamber pressure was measured after firing with a mercury manometer. Time-lapse photographs were taken of the manometer and an adjacent stopwatch to obtain a record of the pressure. The results for four tests are shown in Figure A1.

The first pressure measurements were obtained five seconds after firing. The excess pressure was typically 125 mm Hg. This is close to the anticipated initial over-pressure of 141 mm Hg (see Table A2). The average decay rate was $53\% \text{ min}^{-1}$, although some differences were observed between tests.

The temperature of the exhaust gas was measured by means of a single thermistor probe placed ~ 60 cm from the chamber wall and ~ 1 m to the side of the rocket. The results for two tests are shown in Figure A2.

The first temperature readings were obtained 30 seconds after firing, due to limited response time of the thermistor. The initial temperature readings were 28 and 24°C above ambient for tests 6 and 8, respectively. This is substantially less than the 72°C temperature jump anticipated (see Table A2), probably due to large heat transfer to the rocket housing and to the chamber walls within the first 30 seconds

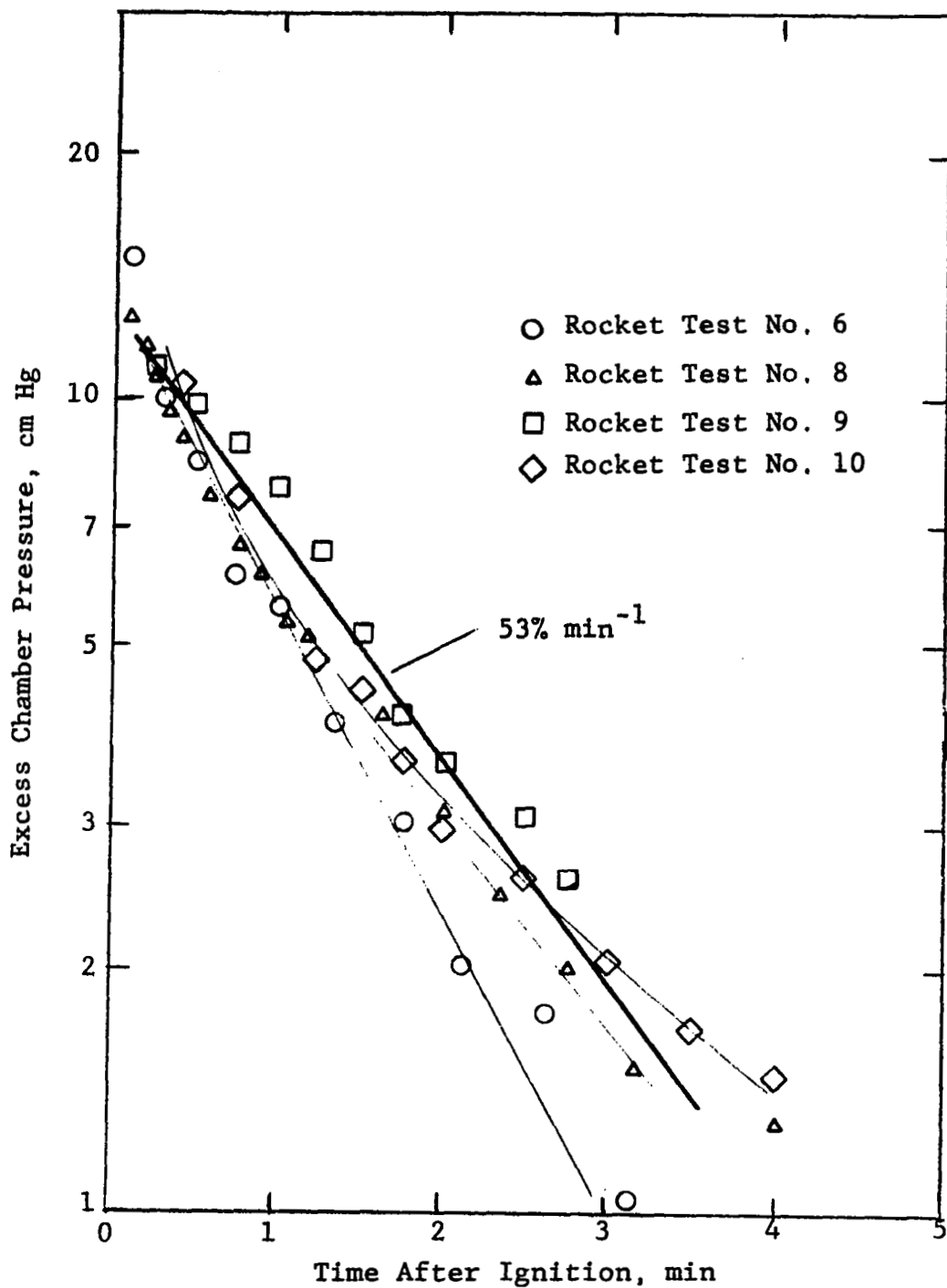


Figure A1
CHAMBER EXCESS PRESSURE AFTER ROCKET IGNITION

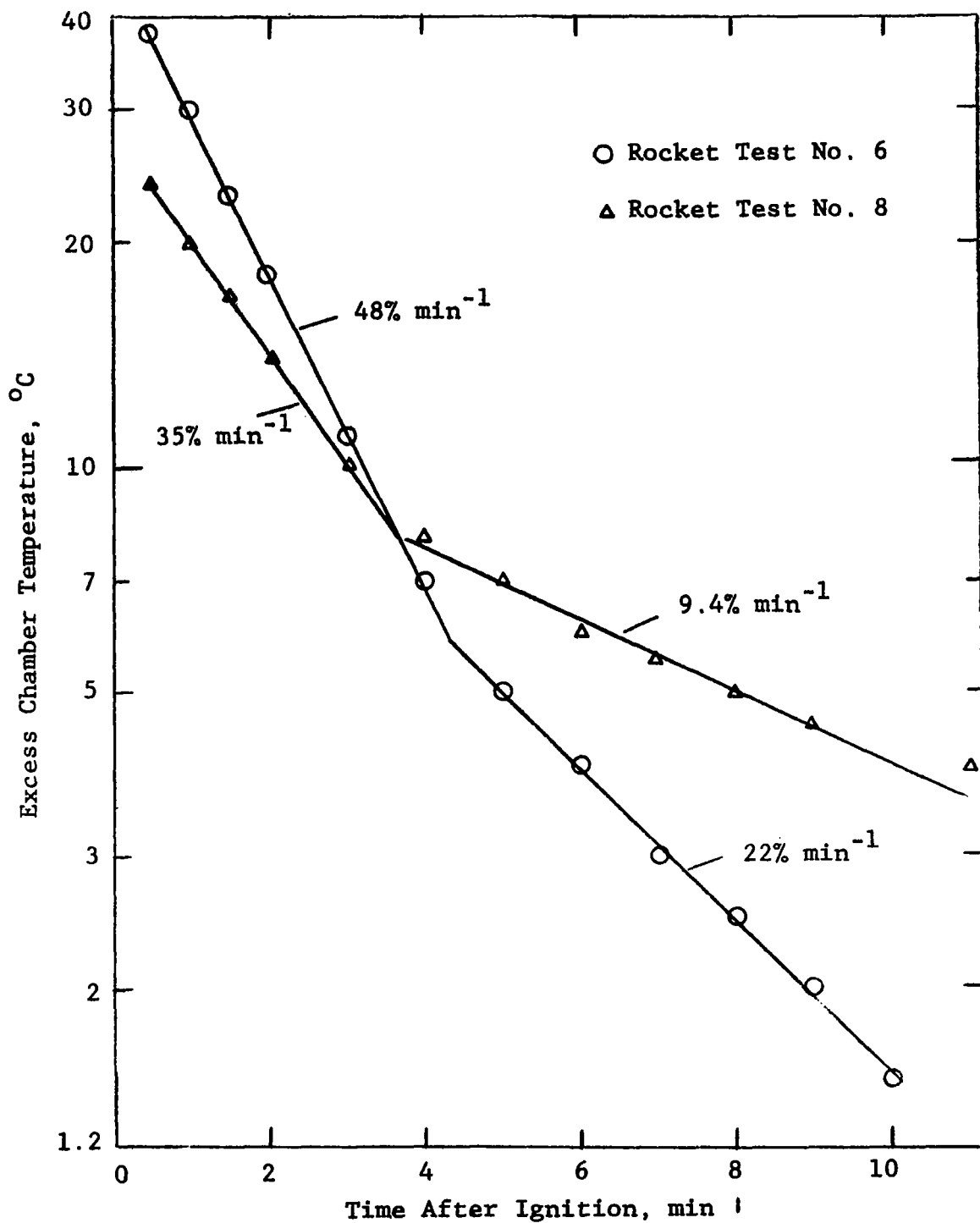


Figure A2
CHAMBER EXCESS TEMPERATURE AFTER ROCKET
TEST NO. 6 AND NO. 8

after firing. The rate of excess temperature decay during the first four minutes was 48 and 35% min^{-1} for tests 6 and 8, respectively. Both rates are lower than the corresponding pressure decay rates, suggesting chamber leaks. A leak was, in fact, observed in test 6, where a valve was inadvertently left open.

The temperature decay curves in Figure A2 exhibit a break in slope at about four minutes. This coincides with the return of the pressure to ~ ambient (see Figure A1), suggesting that chamber leakage and the resulting adiabatic cooling played a role in the first four minutes.

In Figure A3, the temperature data for test 8 is carried out to 40 minutes. It is seen that the slope of the curve decreases further with increasing time. The rate of decrease in the 15 to 40 minute time span is 3.4% min^{-1} .

4.2 Chamber HCl Measurement

The chamber HCl concentration in tests 6-11 was measured by distilled-water bubblers located inside the chamber. Three consecutive samples, 20 minutes each, were taken for each test. In tests 6-8, the first bubbler sample was started immediately after firing. In tests 9-11 the chamber contents were diluted with room air after the rocket firing. For these tests, the bubbler sampling sequence was started after the dilution was concluded.

After retrieval from the chamber, the inlet tube was washed down to collect all the HCl. The contents were analyzed for chloride ions and pH. These two measurements agreed well, on the average.

The HCl concentration measurement results for test 6-8 are plotted in Figure A4. The HCl concentrations are expressed in ppm by volume, appropriate for gaseous trace constituent, although it is not known that the HCl is in the form of a gas.

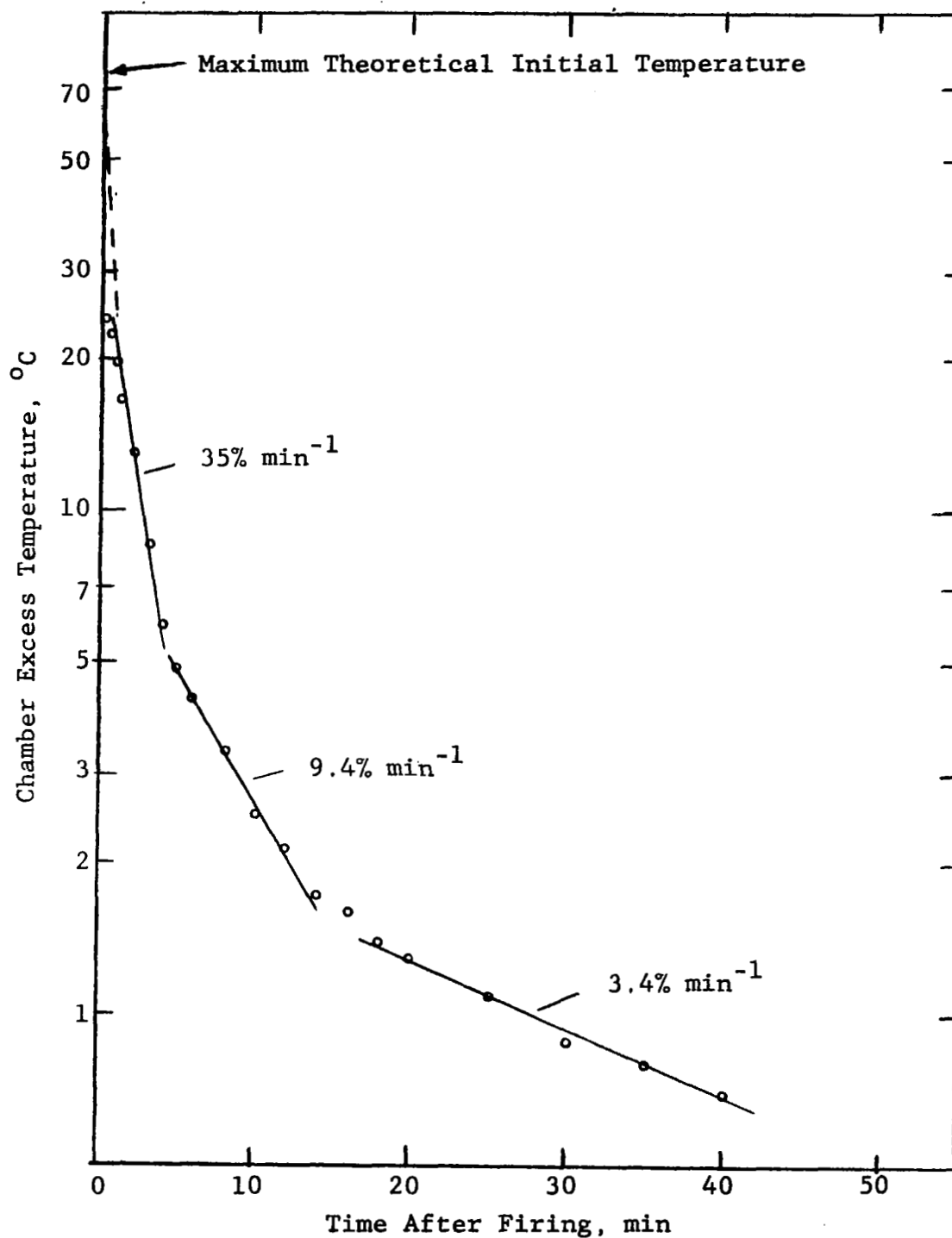


Figure A3

DECAY OF CHAMBER EXCESS TEMPERATURE IN TEST NO. 8

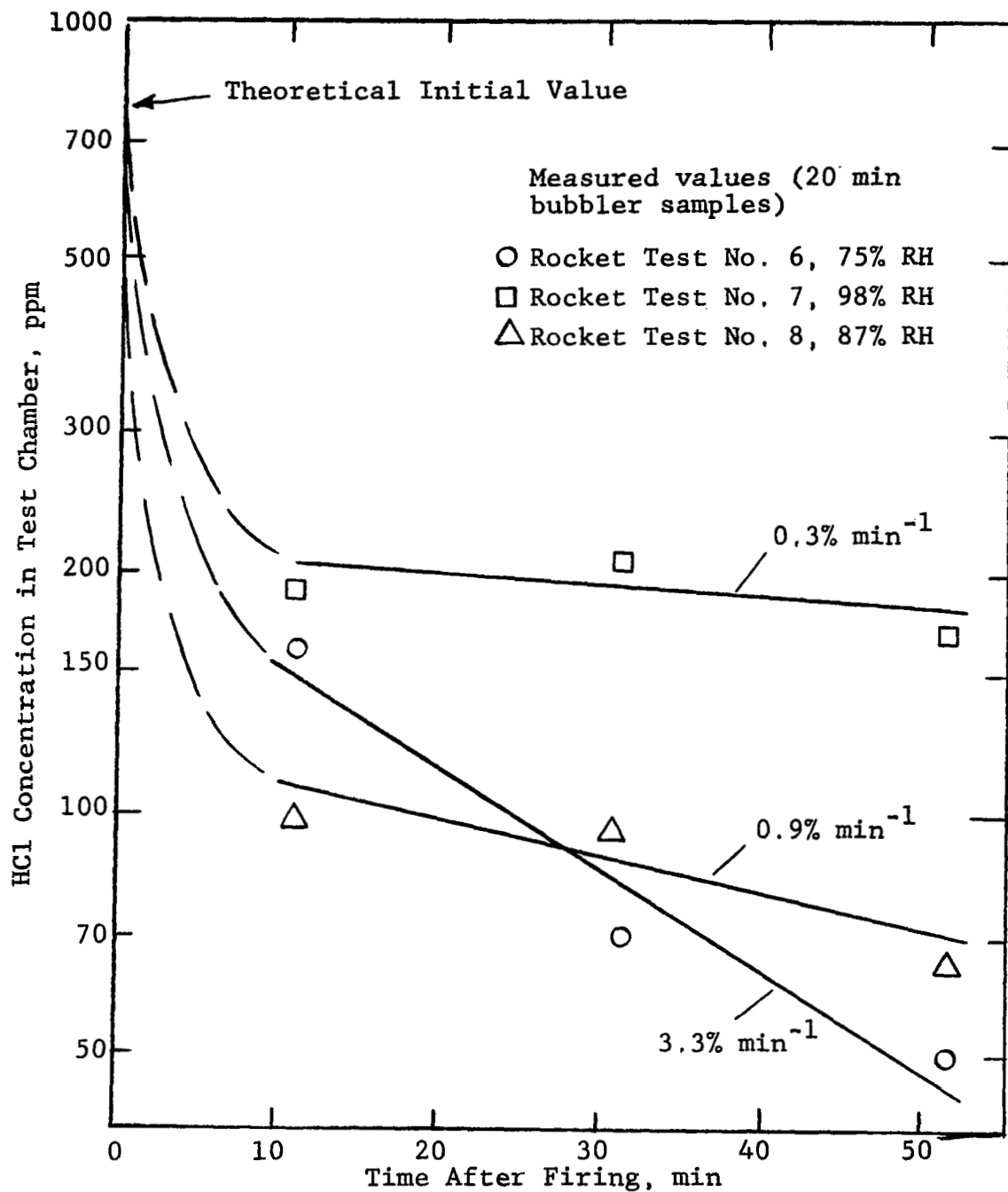


Figure A4

HCl CONCENTRATION IN CHAMBER FOR TESTS 6-8

Figure A4 shows two striking features. First, the measured HCl concentration is much lower than anticipated in Table A2. The point plotted at 10 minutes is from 12 to 25% of the anticipated concentration. Second, the decay rate over the period 10-50 minutes is exceedingly small.

The low HCl concentration obtained at the 10 minute point indicates an initial rapid loss of HCl to the wall: 75 to 88% is transferred in the first few minutes after firing. It is of interest to note in Figure A2 that the temperature drops by a similar amount in 4 to 6 minutes. In view of the known parallelism (A7) between convective heat transfer and convective mass transfer, the sharp initial drop of HCl concentration can be explained by rapid absorption on the wall, analagous to the rapid temperature drop. The bubbler system used did not have sufficient time resolution to follow the initial rapid drop in HCl concentration.

The second remarkable feature of Figure A4 is the low rate of decrease of HCl concentration during the time span 10 to 50 minutes. The rates in Figure A4 are 0.3 to 3.3% min⁻¹. The rate of test 8 was 0.9% min⁻¹, less than the rate of temperature decrease over the same time period (Figure A3). Two possible explanations for the slow HCl loss are: 1) saturation of the wall, and 2) droplet formation.

In tests 9-11, the chamber was vented prior to the HCl measurement. The objective was to decrease the HCl concentration present at the time of the scavenging experiment. The results of the HCl measurements for these tests are shown in Figure A5.

Figure A5 shows that for tests 9 and 10, the venting accomplished the desired result: the initial measured HCl concentrations were 120 and 25 ppm for tests 9 and 10, respectively. The observed change of HCl concentration with time, however was unexpected: for both tests 9 and 10, the HCl concentration increased to ~ 200 ppm within 30 minutes

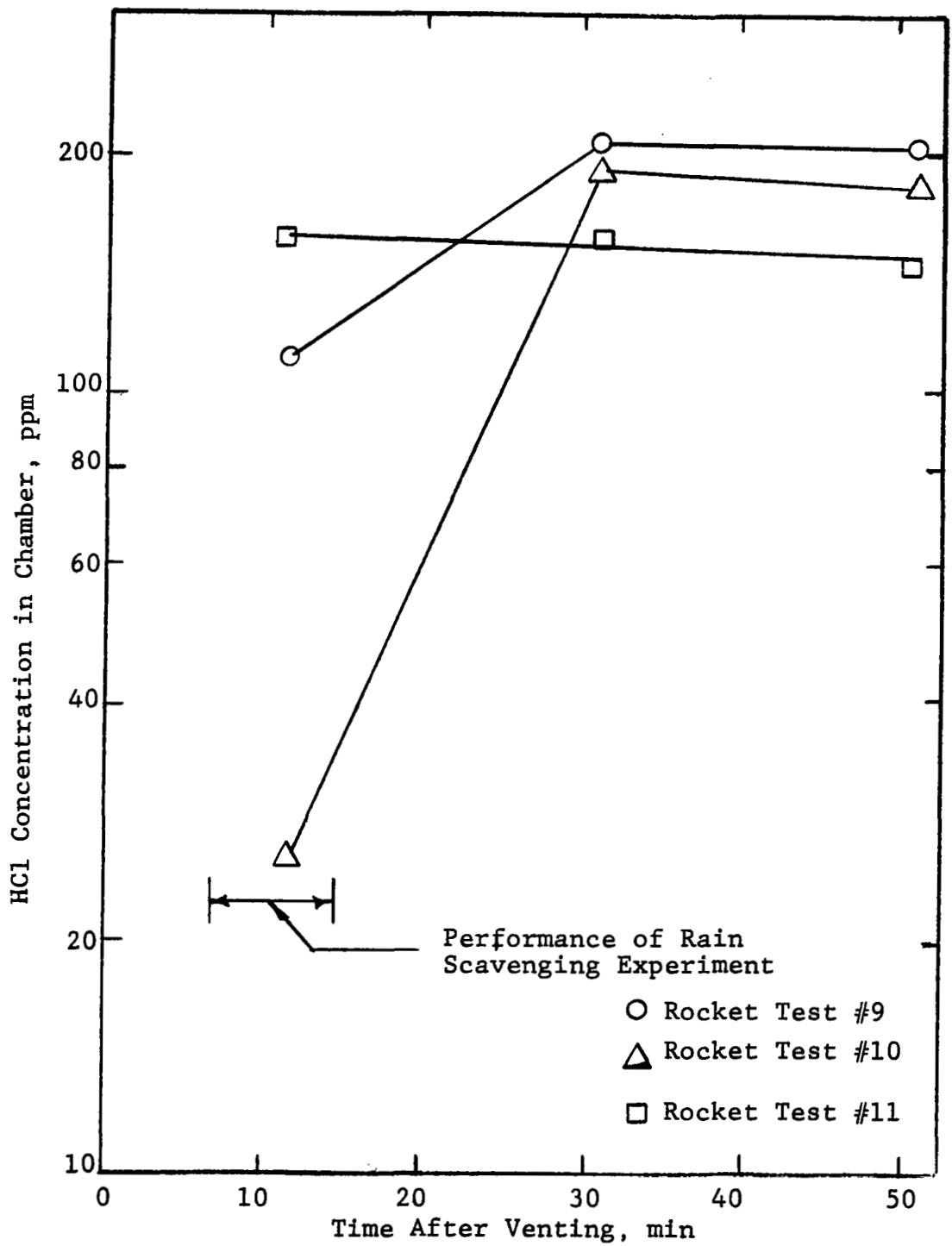


Figure A5

CONCENTRATION OF HCl IN CHAMBER

after venting. This increase of HCl concentration can only be due to gradual desorption of HCl from the chamber walls, after venting.

The HCl measurements in tests 9 and 10 show that HCl absorption on the chamber wall is, to a large extent, a reversible process. Upon dilution with room air, which lowered both the HCl concentration and relative humidity within the chamber, HCl was released from the wall and an equilibrium level at ~ 200 ppm was established. The reversibility of HCl wall absorption indicates that a moisture film on the wall is involved in the process. We note that a water film 5 μm thick on the wall (~ 500 g H_2O , total) would be sufficient to absorb 80% of the total HCl.

Test 11, although run as a duplicate of test 10, did not demonstrate the lowered initial HCl concentration. As discussed in the body of this report, we suspect an error in the initial bubbler measurement for this test.

4.3 Measurements of Chamber Al_2O_3 Concentration

In each test, the mass concentration of Al_2O_3 particles in the chamber was measured by sampling with an Anderson cascade impactor (Anderson Viable Particle Sampler, 2000 Inc., Atlanta, Georgia). This device obtains the mass concentration of particles in six size ranges.

The Anderson sampler was located inside the chamber and had a short, right angle inlet of 1.27 cm diameter. The sampling criteria of Davies (A9) show that 100% sampling efficiency was assured for particle size up to 2.1 μm diameter. A particle density of 4 g/cc was assumed in using Davies' criteria.

The sampling period used with the Anderson sampler was 10 or 20 minutes. The samples (one per test) were drawn at various times after rocket firing or chamber venting.

The mass catch on each of the six collection stages was determined gravimetrically after dessicating the sample at room temperature. The results are shown in Table A4.

Table A4 shows (extreme right column) that the measured Al_2O_3 mass concentration was never more than 0.72 g/m. This value was obtained in test 6, where the sample was taken shortly after firing. This value is comparable to values obtained in previous tests (not discussed in this report), and is approximately 50% of the expected Al_2O_3 mass concentration (Table A2).

The measured Al_2O_3 mass concentrations in Table A4 indicate a low rate of loss to chamber walls during the time period 5 to 40 minutes. The loss rate over this period was about $1.0\% \text{ min}^{-1}$. Previous tests, in which more than one Al_2O_3 sample was taken per test, indicated comparable loss rates.

The cumulative size distribution by mass, plotted from the data in Table A4, is shown for tests 6-11 in Figure A6. The mass median diameter was 2.0 to 2.5 μm for tests 6-8 (no chamber venting) and 1.2 to 2.0 μm for tests 9-11 (chamber venting).

It is noted that the observed loss rate of Al_2O_3 particles is comparable to the expected loss rates for 2.0 μm particles under conditions of mild stirring (see Table A3). Table A3 also shows that particles of diameter greater than 7 μm would drop out at such a rate (~ 40% loss in five minutes) that they would largely be missed by the Anderson sampler.

The low loss rate in the time period 5-40 minutes makes Al_2O_3 particles a useful measure of the degree of venting in tests 9-11. The measured mass concentrations in tests 9-11 should be compared to the average for tests 7 and 8 (not vented), which were sampled in the same time period. By this index, the amount of dilution achieved in tests 9, 10, and 11 was 55%, 82%, and 91%, respectively.

Table A4

ANDERSON IMPACTOR PARTICLE SIZE RESULTS
 Mass collected (mg) on stage with percentage of total mass collected in parentheses

Rocket Test Number	Sampling Time (min)							Total (mg)	Particulate Mass
		Stage 1 Above 9 μm	Stage 2 5.5-9 μm	Stage 3 3.3-5.5 μm	Stage 4 2-3.3 μm	Stage 5 1-2 μm	Stage 6 Below 1 μm		Conc (g/m^3)
6	2-12	8.8 (4.3%)	6.5 (3.2%)	59.6 (29.3%)	58.7 (28.9%)	48.8 (24.0%)	20.8 (10.2%)	203.2	0.721
7	31-51	11.0 (2.9%)	7.4 (2.0%)	41.6 (11.0%)	144.4 (38.1%)	142.3 (37.6%)	32.1 (8.5%)	378.8	0.672
8	35-45	6.7 (5.3%)	4.1 (3.2%)	9.0 (7.1%)	41.5 (32.9%)	49.5 (39.2%)	15.4 (12.2%)	126.2	0.448
9*	35-45	3.4 (4.7%)	3.3 (4.6%)	4.6 (6.4%)	10.4 (14.5%)	32.6 (45.5%)	17.4 (24.3%)	71.7	0.255
10**	27-37	1.6 (5.7%)	1.7 (6.1%)	1.8 (6.5%)	2.2 (7.9%)	15.0 (53.8%)	5.6 (20.0%)	27.9	0.099
11**	34-44	2.5 (17.2%)	2.0 (13.8%)	1.6 (11.0%)	1.6 (11.0%)	2.4 (16.6%)	4.4 (30.3%)	14.5	0.052

* Chamber vented 5 minutes.

** Chamber vented 15 minutes.

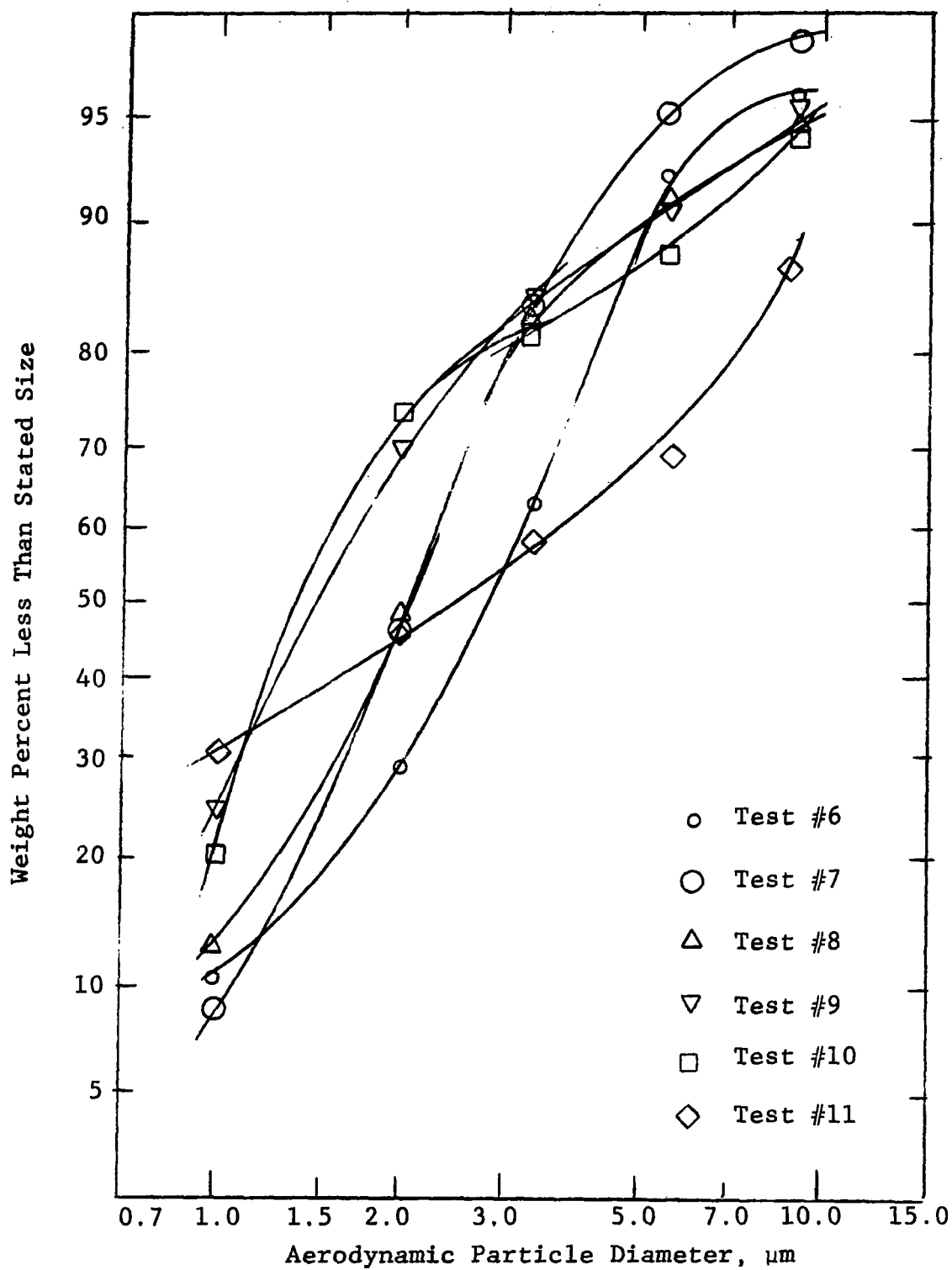


Figure A6

Al_2O_3 PARTICLE SIZE DISTRIBUTIONS

5. CONCLUSIONS

The data presented and discussed in this Appendix show that the low initial value obtained for the HCl concentration in each test was due to rapid transfer of HCl to the wall in the first few minutes after firing. This rapid drop of HCl concentration is entirely consistent with the measured rapid drop in temperature during the initial 4 to 6 minutes. The initial rapid drop in HCl concentration was not observed directly, due to the limited time resolution of the bubblers use to determine HCl concentration.

The Al_2O_3 mass concentration within the chamber also decreased rapidly during the first few minutes after firing, probably due to rapid fall-out of the largest particles. From ten minutes after firing onward, however, the rate of loss was very slow, $\sim 1\% \text{ min}^{-1}$. The observed rate agrees well with the theoretical rate for loss of $2 \mu\text{m}$ Al_2O_3 particles by sedimentation.

Subsequent to the initial rapid loss of chamber HCl, a period ensued in which the rate of HCl loss was very slow. The HCl loss rate during the period 10 to 50 minutes after firing was significantly less than the rate of decrease of excess temperature, but comparable to the rate of fall-out of Al_2O_3 particles. In this respect, HCl remaining airborne in the 10 to 50 minute period behaved like droplets. However, since saturation of the chamber wall could also produce a slow HCl loss rate, it cannot be concluded from the present data that acid droplets actually formed within the chamber.

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Appendix B

MASS BALANCES FOR ROCKET EXHAUST HCl AND Al_2O_3

MASS BALANCES FOR ROCKET EXHAUST HCl AND Al_2O_3

1. DIRECT MEASUREMENT OF HCl AND Al_2O_3 DEPOSITION ON CHAMBER WALLS

In addition to the measurements of airborne HCl and Al_2O_3 described in Appendix A, certain direct measurements were made of the deposits on the chamber walls. These are described below.

HCl absorption by the wall and other surfaces was investigated by three techniques:

1. After complete chamber venting, a pre-selected area of the wall was washed repeatedly with cellulose filter "swab". The wash water was analyzed for chloride.
2. After complete chamber venting, the chamber interior was washed using the hot-water spray-down system. An aliquot was analyzed for chloride.
3. A metal coupon, painted to resemble the chamber wall, was exposed briefly to the exhaust cloud, then retrieved and washed. The wash was analyzed for chloride ion.

In the swabbing technique, a pre-designated 20 x 20 cm area of the chamber wall was washed successively with four wetted cellulose filters. The filters were handled with rubber gloves. Each filter was placed in 20 ml of distilled water. Analysis of the water showed that successive washings removed decreasing amounts of chloride ion. A significant amount, however, was removed even by the fourth filter. The total removal in tests 8-10 was 5.1 to 6.7 mg. When extrapolated from the 400 cm^2 area to the entire chamber wall, this amounts to 15 to 16 g HCl. For comparison, the HCl produced in the rocket fuel combustion is 98.0 g (see Table A1 of Appendix A).

The second study of the HCl remaining on the chamber after complete venting was done in tests 9 and 10 with the chamber wash-down system. About 700 l of hot tap water was

sprayed on the chamber walls. An aliquot of this wash was taken for chloride ion analysis. A blank was used to correct for tap water chloride ion background. The amount of chloride ion recovered by the wash was 51 g and 35 g for tests 9 and 10, respectively. By comparison with the results of the swab test, it is seen that the full chamber wash down with hot water is more efficient at retrieving chloride ion than the swab tests with cold distilled water.

As a check on the amount of HCl absorbed on the wall after firing but prior to any venting, a coupon experiment was conducted during test 11. A steel coupon, 1.0 x 5.2 x 17.5 cm, was painted with an oil-base enamel similar to that on the chamber wall. This coupon was inserted into the chamber through a small access door two minutes after firing during test 11. It was retrieved after 10 minutes of exposure and immediately placed into a large beaker of water. The purpose of the water bath was to dissolve HCl from the coupon and dilute it to prevent its loss.

Analysis of the coupon beaker water showed that 9.9 mg of chloride ion were absorbed by the coupon in its 10 minute exposure to the exhaust cloud. Extrapolation of this amount to the entire wall area of the chamber showed that the wall would absorb 42.6 g HCl in the same period of time.

The results of the wall absorption tests are shown in Table B1.

It was noted that the wash waters from the swab tests, full chamber wash downs, and the coupon experiment were deficient in H^+ concentration, relative to the Cl^- concentration. The difference between pH and pCl was 1.64 for the swab tests (average of 18 tests), 2.14 for the coupon test, and 5.31 for one full-chamber wash down. These differences between pH and pCl is in marked contrast to the results for the bubbler samples, rain samples, and rain blanks, for which the average differences were near zero. The deficiency in H^+ relative to

Table B1

VALUES FOR HCl WALL ABSORPTION IN TEST CHAMBER (g HCl)

	<u>Rocket Test Number</u>			
	<u>8</u>	<u>9</u>	<u>10</u>	<u>11</u>
Filter Paper Washing* (g HCl)	14.2	14.7	16.3	-
Subsequent Chamber Washing** (g HCl)	-	50.9	35.2	-
Coupon Experiment*	-	-	-	42.6
Venting Time Interval Before Rain Scavenging Experiment (min)	0	5	15	15

* Extrapolated to entire chamber wall area from measured absorption on a small area (400 cm² for the filter paper swab tests, 227 cm² for the coupon test).

** Determined from an aliquot of the wash water.

NOTE: Theoretical total HCl = 98.6 g

Cl^- indicates a neutralization of H^+ at the walls.

The Al_2O_3 deposition in the chamber was evaluated in test 9 by means of microscope slides set out at the bottom of the chamber. This was prompted by the observation that all upward facing surfaces were heavily coated with a white powder after each test. The downward facing surfaces had much less deposit. The preferential deposition on upward facing surfaces supports the discussion in Section 3 of Appendix A, in which particle deposition was assumed to occur primarily by sedimentation.

Photomicrographs of one slide are shown in Figure B1. It is seen that the largest individual particles are 5 μm in diameter. The appearance of particle flocks on the slide suggests that the particles settled onto the slide as aggregates.

One slide was weighed, then washed and reweighed to determine the mass deposit. The deposit was 3.3 mg. Extrapolation of this amount to the entire upward-facing area of the chamber yielded the value 63.8 g for the total deposit.

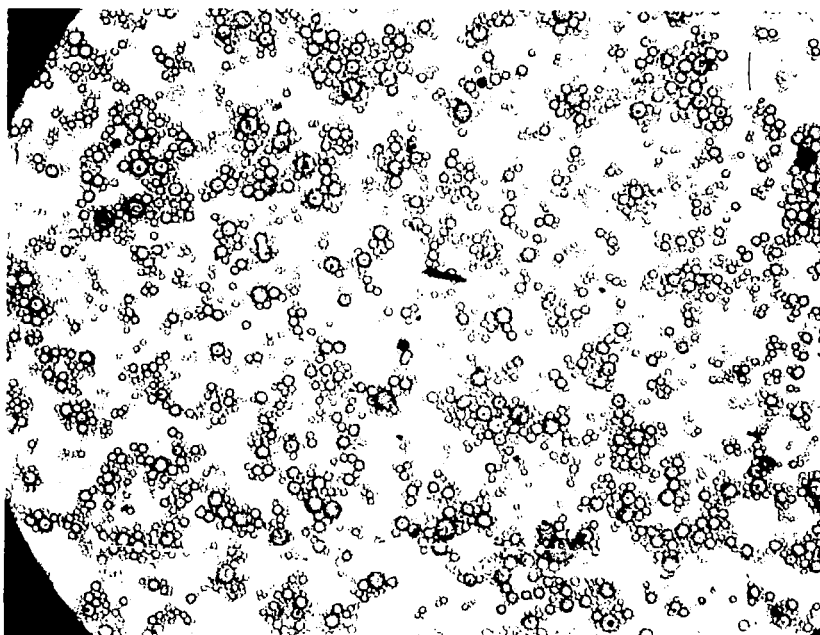
2. HCl MASS BALANCE

In this section, we shall summarize the data available on the mass balance of HCl. More properly, the data presented pertain to the mass balance on chloride ion, since this was the species actually measured. As discussed in the last section, the balance of H^+ ions might be quite different.

Table A1 of Appendix A showed that the rocket motor fuel contained 96.0 g of chlorine. It is assumed that this appears in the chamber as a soluble chloride, either HCl or another substance formed at the wall.

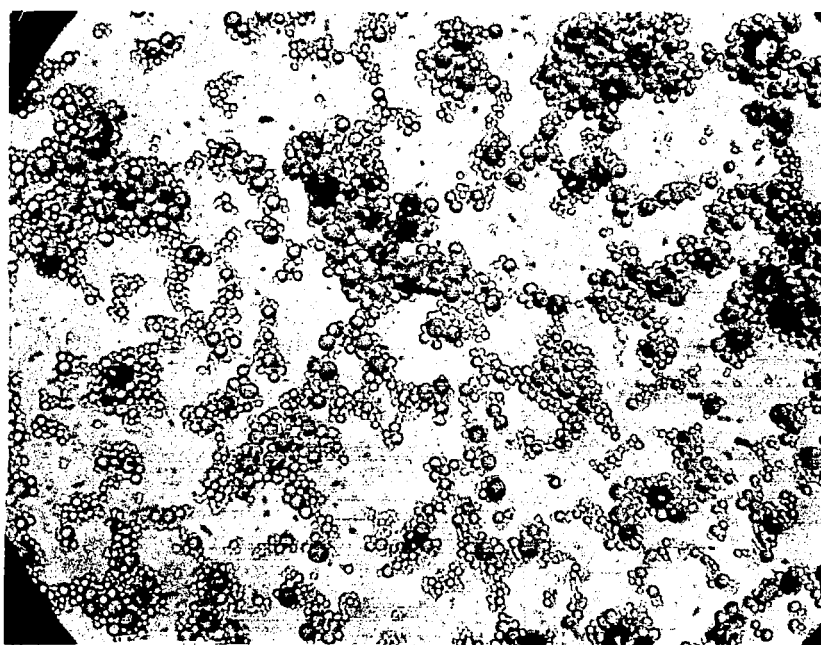
The data presented in Appendices A and B show that the disposition of the chloride in each test is as follows:

1. Cl^- removed from chamber by initial venting (tests 9, 10, and 11 only)
 - a. airborne Cl^- removed



Magnification = 420

— 10 μ m



Magnification = 810

— 10 μ m

Figure B1

PHOTOMICROGRAPHS OF SETTLED Al_2O_3 DUST FOR TOCKET TEST NO. 9

- b. Cl^- spontaneously released from wall during venting
 2. Cl^- removed from chamber by the rain sample, rain blank, bubblers, distilled water beakers, etc.
 3. Cl^- removed from chamber by the final venting .
 - a. airborne Cl^- removed
 - b. Cl^- spontaneously released from wall during venting
 4. Cl^- chemically bound to wall, but removable by a hot water wash
 5. Residual Cl^- on wall, not removable by washing

Item 1a can be determined from the Cl^- concentration in the chamber just prior to venting and the amount of dilution achieved by venting. The Cl^- concentration present prior to venting can be estimated for test 9, 10, and 11 from the average of the first bubbler measurements in tests 6, 7, and 8. The dilution is known from measurements on the Al_2O_3 (see Section 4.3 in Appendix A). The results are shown in Table B2.

Item 1b of the Cl^- budget is included as a separate item as the result of observations made in tests 9 and 10. In these tests (see Section 4.2 of Appendix A), Cl^- release from the wall was demonstrated by an increase in airborne Cl^- after venting was concluded. The released species was obviously a gas, i.e., HCl . The amount of release which occurred during venting is not known.

Item 2 of the Cl^- budget may be determined by summing the measured Cl^- content of the rain sample, rain blank, bubbler samples, distilled water beakers, etc. This sum never exceeded 0.1 g HCl . This contribution is negligible.

Item 3a of the Cl^- budget may be determined from the bubbler measurement of airborne Cl^- , taken just prior to final venting. The results are shown in Table A9 of Appendix A. No estimate is available, however, of item 3b.

Table B2
Cl⁻ BUDGET FOR THE CHAMBER TESTS

Item	<u>Amount of Cl⁻, g</u>	
	<u>Test 9</u>	<u>Test 10</u>
1. Amount removed by initial venting		
a. from chamber volume	9.5	17.4
b. released from wall	unk.	unk.
2. Amount removed by experiments (rain sample, rain blank, bubblers, etc.)	neg.	neg.
3. Amount removed by final venting		
a. from chamber volume	31.1	25.5
b. released from wall	unk.	unk.
4. Removed from wall by hot water wash	49.5	34.5
5. Residual on wall	<u>unk.</u>	<u>unk.</u>
Total	90.1	77.4
Theoretical amount from rocket	<u>96.0</u>	<u>96.0</u>
Not accounted for	5.9	18.6

unk = unknown
neg = negligible

The Cl^- which remains on the walls after venting may be partially removed by a hot water wash (Cl^- budget item 4). This wash was done in tests 9 and 10. The results are shown in Table B2. The marked deficiency of H^+ in the wash water indicated that the Cl^- removed was not HCl , but some other chloride.

Table B2 shows that Cl^- budget items 1a, 2, 3a, and 4 account for 90.6 and 77.9 g in tests 9 and 10, respectively. This compares well to the theoretical 96.0 g Cl^- produced by the rocket combustion. The largest budget item was 4, the Cl^- removed from the walls by a hot water wash.

3. Al_2O_3 MASS BALANCE

The mass balance on Al_2O_3 may be checked with the data from test 9. For reference, the theoretical Al_2O_3 production from the rocket burn is 137.3 g (see Table A1 of Appendix A).

The amount of Al_2O_3 removed from the chamber in test 9 by venting may be determined from the data in Table A4 of Appendix A. As discussed in Section 4.3 of Appendix A, 55% of the chamber's contents were removed in the initial venting. The reduction of Al_2O_3 content may be estimated by subtracting the measured Al_2O_3 content in test 9 to the average of the values for the two preceding tests: thus, 0.30 g/m^3 or 26 g Al_2O_3 total were vented. Due to the slow decay rate of Al_2O_3 concentration, it may be assumed that the remaining 0.255 g/m^3 (22 g total) were vented at the conclusion of test 9. Thus, the total vented Al_2O_3 in test 9 is estimated to be 48 g.

The Al_2O_3 deposit on the chamber walls at the conclusion of test 9 was measured as described in Section 4.3 of Appendix A. The result found that there was 64 g Al_2O_3 deposited on upward facing surfaces.

The measured wall deposit and venting losses of Al_2O_3 in test 9 therefore account for 112 g Al_2O_3 . Therefore, 82% of the theoretical Al_2O_3 is accounted for.

4. CONCLUSIONS

It is concluded from the data presented and discussed in this Appendix that a satisfactory mass balance for HCl and Al_2O_3 was achieved in all tests for which mass balance was attempted. In the case of HCl, 94% and 81% of the theoretical amount were accounted for in tests 9 and 10, respectively. For Al_2O_3 , 82% of the theoretical amount was accounted for in test 9.

The fact that a satisfactory mass balance was achieved lends credence to the measurement techniques used for HCl and Al_2O_3 . In particular, the bubblers used to measure airborne HCl concentration apparently result in errors of less than 20%.

Appendix C

ABSORPTION OF HCl ON VARIOUS SURFACES

ABSORPTION OF HCl ON VARIOUS SURFACES

1. INTRODUCTION

The interaction of a solid rocket exhaust cloud with soil, foliage, and water surfaces is determined in part by the absorption characteristics of these surfaces for hydrogen chloride. Thus, absorption characteristics are involved in the environmental impact of solid rocket operations. Absorption characteristics are also important when applying large-scale diffusion codes, which commonly employ the assumption of complete reflection (no absorption) at the terrain surface.

This appendix presents first data on the capability of various surfaces to absorb and retain HCl from a solid rocket exhaust cloud. Three surfaces were studied briefly: a water surface, a sand surface, and a painted steel surface.

2. EXPERIMENTAL METHOD

The three types of surfaces studied with respect to their HCl absorption characteristics were exposed to a confined exhaust cloud produced by firing a 0.454 kg (propellant weight) solid rocket into a 5.49 m diameter spherical chamber. The rocket and chamber are described in the main body of this report. The characteristics of the rocket exhaust cloud are described in Appendix A.

The absorption characteristics of an open water surface were studied by placing 250 ml beakers containing 54 to 193 ml of distilled water at various points within the chamber prior to firing. The beakers were retrieved at the conclusion of the test, after the chamber had been thoroughly flushed with room air. The water was then analyzed for chloride ion content with a specific ion electrode and for hydrogen ion content with a pH meter.

Ottawa sand (Fisher Scientific Company) was used in the study of HCl absorption on sand. A 1100 ml beaker containing a 12 cm deep layer of sand was placed within the chamber on the day prior to test 11. Thus, the sand had sufficient time to equilibrate to the chamber conditions. After the chamber was opened to initiate flushing with room air, 340 ml of distilled water was added to the beaker to prevent escape of the absorbed HCl. The water in the sand beaker was then analyzed for Cl^- and H^+ . An identical beaker of sand, not exposed to the rocket cloud, was used to determine the Cl^- and H^+ contribution from the sand itself.

HCl absorption by a painted steel surface was determined by exposing a 1.0 x 5.2 x 17.5 cm steel coupon painted with an oil base enamel to the exhaust cloud. The coupon was placed within the chamber prior to the rocket firing. Approximately 10 minutes after firing, the coupon was removed from the chamber through an access port and placed in a vessel containing 1627 ml distilled water. The vessel was then capped. Subsequently, the water was analyzed for Cl^- and H^+ .

Further data on HCl absorption by a painted steel surface were obtained by washing down the chamber walls after each test. About 700 l of hot tap water was sprayed into the chamber, after the chamber had been thoroughly flushed with room air. An aliquot of the wash water was taken and analyzed for Cl^- and H^+ . A reference sample of the hot tap water was also analyzed to determine the Cl^- and H^+ background.

3. EXPERIMENTAL RESULTS

The results of the surface HCl absorption experiments are shown in Table C1. To facilitate comparison of the various surfaces, the results are expressed in terms of unit exposed area of the surface. For the sand surface, the exposed area is taken to be the cross-sectional area of the beaker which held the sand.

Table C1

ABSORPTION OF ROCKET EXHAUST HCl BY VARIOUS SURFACES

<u>Surface</u>	<u>Area Exposed to Cloud, m²</u>	<u>Soluble Cl⁻ Absorbed per Unit Exposed Area, g/m²</u>				<u>Average Value of pH-pCl</u>
		<u>Test 8</u>	<u>Test 9^a</u>	<u>Test 10^b</u>	<u>Test 11^b</u>	
Open Water						
near rocket	0.00283	0.86	1.06	0.50	d	
opposite rocket	0.00283	-	1.31	-	-	-0.14
chamber bottom	0.00283	0.11	1.45	0.64	-	
Sand	0.0053	-	-	-	1.41	1.55
Painted Steel						
coupon ^e	0.0227	-	-	-	0.44	2.14
chamber wall	94.7	-	0.54	0.37	-	5.31

^a Chamber vented 5 minutes early in test to reduce HCl concentration.

^b Chamber vented 15 minutes early in test.

^c Three beaker locations: on catwalk near rocket; on catwalk opposite rocket; on chamber bottom.

^d Sample lost.

^e Exposed to cloud for 10 minutes only; all other surfaces exposed for full test period.

Table C1 suggests that the amount of HCl absorbed by the open water surface varied from test to test and from location to location in the chamber. This is only partly true. It was noted subsequently that the beakers contained differing amounts of water and that the amount of HCl absorbed increased with the amount of water. This effect was not due to saturation of the water with HCl, since the highest weight fraction HCl observed was 0.2%. (The corresponding HCl vapor pressure is much less than 0.00008 mm Hg.) The effect of container shape and amount of filling is not understood and was not appreciated in these first absorption experiments. Hence, the results in Table C1, at least those for the open water and sand surfaces, must be taken as indicative, not definitive.

Table C1 suggests that the sand surface is at least as effective as water in absorbing HCl. To some extent, the relatively high absorption observed for sand may be due to the fact that a larger beaker was used for the sand than the water, and that a larger volume of sand than water was used. In spite of this uncertainty, it is likely that a sand bed absorbs HCl approximately as well as water. The relatively porous structure and high total surface area of a sand bed would promote strong HCl absorption.

The results in Table C1 also show that painted steel surfaces can absorb substantial amounts of HCl. The painted steel surfaces (no container) were exposed more intimately to the exhaust cloud than were the water or sand surfaces. Hence, comparison of results must be made with caution. It appears, however, that painted steel surfaces absorb significantly less HCl than water or sand.

It was noted in the tests that painted steel surfaces withstood the exhaust cloud well, but bare steel surfaces corroded and rusted rapidly.

The extreme right column of Table C1 compares the measured concentrations of H^+ and Cl^- in the water used to extract HCl from the various surfaces. The quantity tabulated is pH-pCl, where pCl is defined by analogy with the usual definition for pH. It is seen that for the water surface, the observed H^+ and Cl^- concentrations are nearly in balance: the geometric mean ratio of H^+ ions to Cl^- ion is $10^{+0.14} = 1.38$. For the remaining surfaces, however, the extraction water was deficient in H^+ as compared to Cl^- . For the chamber wall wash, Cl^- outnumbered H^+ by a factor of 204,200. This unbalance of H^+ and Cl^- indicates that a chemical conversion of HCl occurred for the sand and painted steel surfaces.

4. CONCLUSIONS

The first absorption experiments presented and discussed herein indicate that open water surfaces and sand surfaces absorb HCl from solid rocket exhaust clouds, with approximately equal efficiency. A painted steel surface also absorbs HCl, although less than the open water or sand surface.

The effect of HCl dosage on the amount of HCl absorbed was not investigated in the present study. If it is assumed that absorption is proportional to dosage, the present results can be scaled down to estimate the absorption which would occur from an unconfined exhaust cloud. The HCl concentration in these tests was of the order 100 times that which might occur at ground level in an unconfined exhaust cloud and the time of exposure was about 10 times the typical time of passage of an unconfined cloud. Thus, a reduction factor of 1000 should be applied to the present results. In this way, it is estimated that the HCl deposition on open water or sand surfaces from a solid rocket exhaust cloud is of the order 1 mg/m^2 . More work is needed to establish the deposition for typical ground cloud HCl concentrations and times of passage.